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SP88-020

INVESTIGATION OF PROCESS CONDITIONS FOR THE SYNTHESIS OF LIQUID DISTILLATES FROM LIGHT OLEFINS AND METHANOL

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FINAL REPORT

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EXECUTIVE SUMMARY

Due to the anticipated legislative removal of synthetic octane improvers such as TEL and MMT from gasoline, process conditions for the production of Methyl Tertiary Butyl Ether (MTBE), Tertiary Amyl Methyl Ether (TAME) and Tertiary Hexyl Methyl Ether (THME) from C_4, C_5 and C_6 FCC olefinic feedstocks respectively and methanol has been investigated as a means of restoring lost octane quality potential.

MTBE gasoline product quality parameters were determined to be as follows:

Research Octane Blending Number	= 116
Motor Octane Blending Number	= 101
Reid Vapour Pressure (Additional n-Butane Requirement for 10% MTBE Blend)	= 1.0%
Distillation Restriction	= 15% max.

TAME gasoline product quality parameters were determined to be as follows:

Research Octane Blending Number	= 106
Motor Octane Blending Number	= 99
Reid Vapour Pressure (Additional n-Butane Requirement for 10% TAME Blend)	= 1.0%
Distillation Restriction	= 25% max.

C_5 reactor effluent gasoline product quality parameters determined and calculated for the 43.5% isoamylene process conversion to TAME were as follows:

C_5 Reactor feed 25-50% (RON/MON)	= 95.3/84.0
C_5 Reactor Product (RON/MON)	= 96.3/85.8
Reid Vapour Pressure (Reduction in n-Butane Content for 10% Blend)	= 1.%
Distillation Restriction	= 25% max.

THME gasoline product quality parameters were determined to be as follows:

	RON	MON
THME (pure)	90.0	82.0
C_6 Olefin Feed Stream	92.5	80.6
C_6 Reactor Product	92.5	81.6
C_6 Unreacted Hydrocarbons	90.9	79.8

Computerized linear programming (LP) involving a typical Canadian refinery was used to economically assess the value of the produced ethers as octane enhancers for gasoline. Future forecasts relating to the FCC-derived ether compounds were interfaced with a Dept. of Energy, Mines and Resources study carried out by Hycarb Engineering Ltd. (1).

The LP study cases carried out in this investigation indicated the following:

1) Production of MTBE and subsequent gasoline octane enhancement was not economically practical in this study due to octane upgrading competition for FCC C_4 olefins with alkylation processing.

2) TAME processing indicated a small profit under the present refinery design with the TEL and MMT anti-knock additives being allowed into gasoline. The savings were essentially due to the reduced TEL and MMT requirements and showed an after-tax return on investment in about 4 years.

3) LP economic predictions for THME were not carried out, as virtually no octane improvement was recorded for THME over the FCC C_6 ether precursors from which the oxyfuel was originally derived.

4) Following the removal of MMT and TEL as octane enhancers, the installation of an isomerization process was necessary to upgrade the LSR naphtha octane quality and allow for the continued use of this stream as a gasoline blending component.

5) Following the installation of the isomerization process, the study case refinery possessed sufficient octane capability as to dispense with both ether processing and anti-knock additive octane enhancement.

6) The economics of on-site refinery FCC-derived MTBE is related to the available supply of C_4 olefins. Refineries which have undersized alkylation plants or produce excess olefins i.e. from adjoining petrochemical steam crackers or by high severity -high octane catalyst FCC operation appear to have economic advantage over the study case refinery.

7) The role of MTBE and TAME purchase or on-site refinery FCC-derived production may reside in the application of a final octane trimming operation or as a high octane additive to a specialty product.

SOMMAIRE-RECOMMANDATION

En prévision de l'adoption d'une loi visant à éliminer de l'essence les antidétonnants synthétiques tels que le plomb tétraéthyle (PTE) et le MMT, on a étudié les conditions des procédés pour la production d'éther butylique tertiaire de méthyle (EBTM), d'éther amylique tertiaire de méthyle (EATM) et d'éther hexylique tertiaire de méthyle (EHTM) à partir, respectivement, de charges d'alimentation oléfiniques C_4, C_5 et C_6 obtenues par craquage catalytique fluide (CCF) et de méthanol. Ces études avaient pour but de trouver un moyen de compenser la diminution de l'indice d'octane occasionnée par l'élimination des antidétonnants.

Les paramètres relatifs à la qualité des essences à l'EBTM ont été établis comme suit :

Indice d'octane recherche	= 116
Indice d'octane moteur	= 101
Tension de vapeur Reid (n-butane supplémentaire pour mélange contenant 10 % d'EBTM)	= 1,0 %
Restriction sur la distillation	= 15 % max.

Les paramètres relatifs à la qualité des essences à l'EATM ont été établis comme suit :

Indice d'octane recherche	= 106
Indice d'octane moteur	= 99
Tension de vapeur Reid (n-butane supplémentaire pour mélange contenant 10 % d'EATM)	= 1,0 %
Restriction sur la distillation	= 25 % max.

Les paramètres relatifs à la qualité des essences effluentes du réacteur de C_5, déterminés et calculés en fonction de la conversion à 43,5 % de l'isoamylène en EATM, sont les suivants :

Charge d'alimentation C_5 (de 25 à 50 %) (IOR/IOM)	= 95,3/84,0
Produit C_5 effluent du réacteur (IOR/IOM)	= 96,3/85,8
Tension de vapeur Reid (réduction de la teneur en n-butane pour mélange à 10 %)	= 1 %
Restriction sur la distillation	= 25 % max.

Les paramètres relatifs à la qualité des essences à l'EHTM ont été établis comme suit :

	IOR	IOM
EHTM (pur)	90,0	82,0
Charge d'alimentation oléfinique C_6	92,5	80,6
Produit C_6 effluent du réacteur	92,5	81,6
Hydrocarbures C_6 non convertis	90,9	79,8

Un logiciel de programmation linéaire (PL) portant sur une raffinerie canadienne type a permis d'évaluer, d'un point de vue économique, la valeur des éthers produits pour améliorer l'indice d'octane des essences. Les prévisions relatives aux éthers dérivés du CCF ont été comparées aux résultats d'une étude du ministère de l'Énergie, des Mines et des Ressources effectuée par Hycarb Engineering Ltd. (1).

L'étude en PL nous a permis de tirer les conclusions suivantes :

1) La production d'EBTM et son utilisation comme antidétonnant pour l'essence ne s'est pas révélée une solution viable du point de vue économique, en raison de la concurrence, en ce qui a trait aux oléfines C_4 obtenues par CCF, entre l'amélioration de l'indice d'octane et le procédé d'alkylation.

2) La production d'EATM s'est révélée légèrement rentable dans les conditions de production actuelles de la raffinerie, qui permettent l'utilisation des antidétonnants PTE et MMT. Les économies étaient attribuables principalement à la diminution des quantités de PTE et de MMT nécessaires. Le procédé permettait d'obtenir un rendement du capital investi, après impôt, au bout de quatre ans.

3) Les prévisions économiques établies par PL n'ont pas été effectuées pour l'EHTM puisque aucune amélioration sensible de l'indice d'octane n'a été observée par rapport aux C_6 obtenues par CCF dont il a été dérivé.

4) Par suite de l'élimination du MMT et du PTE comme antidétonnants, on devait faire appel à un procédé d'isomérisation pour améliorer l'indice d'octane du naphta léger de première distillation de façon à pouvoir continuer de l'utiliser comme charge d'alimentation dans les mélanges d'essence.

5) Après l'installation du procédé d'isomérisation, la raffinerie sur laquelle portait l'étude était en mesure de produire des essences possédant un indice d'octane suffisamment élevé sans l'utilisation d'éthers ou d'additifs antidétonnants.

6) La viabilité économique de la production d'EBTM par CCF à la raffinerie même est reliée à la disponibilité des oléfines C_4. Les raffineries dont les installations d'alkylation sont de petite taille ou celles qui produisent des excédents d'oléfines (provenant des vapocraqueurs des installations pétrochimiques connexes ou de l'utilisation d'un catalyseur offrant un facteur de sévérité et un indice d'octane élevés dans le procédé CCF) semblent être avantagées par rapport à la raffinerie étudiée.

7) L'EBTM et l'EATM, qu'ils soient achetés ou produits à la raffinerie par CCF, pourraient jouer un rôle dans le réglage final de l'indice d'octane ou pourraient servir d'additifs à indice d'octane élevé dans des produits spécialisés.

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1. INTRODUCTION

1.1 Objectives

The objectives of the present work are as follows:

(a) To investigate process conditions on the individual etherification of C_4, C_5 and C_6 branched olefins from catalytically cracked gasoline.

(b) To evaluate the effect on blending octane number and blending volatility in typical Canadian premium and regular unleaded motor gasolines.

(c) To evaluate blending and economic effects of installing C_4, C_5 and C_6 etherification into a typical Canadian fuels-only refinery using linear programming (LP) and to interface the study to an earlier LP project carried out by Hycarb Engineering for Department of Energy, Mines & Resources (1).

1.2 Justification

Interest in the use of certain high octane number ethers produced from branched olefins containing a tertiary carbon atom adjoining a double bond and methanol stems from three principal thrusts:

(a) The anticipated elimination of traditional metal-based antiknock additives such as lead alkyls and MMT from automotive gasoline blending and consequent loss of octane/barrel potential.

(b) The desire to utilize surplus natural gas via oxidation to methanol as an indigenous source of automotive fuel from a national energy self-sufficiency point of view.

(c) To achieve the objective of (b) without consequential loss of ability to use butane in the gasoline pool or other adverse interactions such as automotive material compatibility problems with methanol itself.

The purpose of the study was to evaluate the production of ethers as an octane improvement process for petroleum fuels, as opposed to the manufacture of chemically pure compounds, especially in the

C_5 and C_6 range. Purification of the reactor effluent from the etherification process was determined solely on the basis of:

(i) effluent quality affecting further downstream processes such as required feedstock quality for C_4 alkylation etc.

(ii) where sufficient remaining unreacted methanol adversely impacted on product quality.

A further consideration was to assess the effect of internal refinery processing of reactable olefins as opposed to the outside purchase of oxygenates allowed in the earlier Hycarb study (1).

1.3 Background

The value in specific circumstances of incorporating certain high octane number ethers formed from olefins and methanol, has been amply demonstrated in the U.S.A., W. Europe, and elsewhere. In the U.S., there was in 1986, 10 000 m^3/d of MTBE capacity already installed with a further 3000 m^3/d scheduled for completion in 1987 (2).

In this study the production of ether compounds and their subsequent octane enhancement have been economically evaluated by linear programming. Linear programming as related to petroleum refining is a computer technique for achieving the most economic approach for raw material purchase, unit operation and total product slate.

Manufacture of MTBE can be considered as a way of incorporating methanol into automotive gasoline without the established undesirable effects on volatility and material compatibility, which direct blending of methanol entails.

Methanol exhibits a high Research blending octane number (124) in unleaded gasolines but this is not paralleled by good Motor Octane performance (99) which results in a very high blending sensitivity. On the other hand, MTBE exhibits a high blending Research ON (116) and high blending Motor ON (101) which is much more desirable.

Methanol addition to unleaded motor gasoline causes a significant non-linear increase in vapour pressure which results in a serious loss of capability to blend surplus butanes directly in to

gasoline. MTBE and TAME actually decrease vapour pressure slightly allowing some additional butanes to be blended into the gasoline while maintaining vapour pressure specification (1,3).

Methanol can easily be extracted from gasoline with water. MTBE is hydrocarbon compatible and does not suffer from this undesirable phenomena particularly in wet petroleum distribution networks. Unlike methanol, MTBE is also compatible with automotive finishes and vehicle fuel system components.

The majority of plants producing MTBE and TAME both in the USA and Europe are associated with petrochemical complexes where naphtha cracking processes produce significant amounts of ether reactive olefins. The concentration of C_4 ether reactive olefin from naphtha crackers is higher (40-50%) than in the corresponding effluent from FCC units in conventional refineries (10-20%) and frequently there is an enhanced chemical - as opposed to fuel - value associated with all or part of the operation which contributes to a favourable economic assessment for ether production (3).

MTBE can be produced directly from natural gas derived butanes as primary feedstocks (4,5,6). This is the basis for the proposed plant in Western Canada to manufacture MTBE and utilize some of the excess methanol (about 5500 m^3/d) and butanes available in Canada for conversion to high octane automotive fuel. Based upon the Houdry linear program economics of such a field gas based process (4,5), MTBE would be about twice as expensive as FCCU or steam cracked derived MTBE. However, Houdry economics relate to a U.S. situation where butanes are in short supply and the logistics of methanol supply and MTBE pipeline movement have not been considered.

An alternate strategy for restoring lost octane barrel capability in a lead-free gasoline blending environment, is to octane upgrade light paraffins by isomerization. LP refinery octane upgrading economics are directly related to the variable computer input data and as a result differing conclusions can occur. Recent studies published by PACE Consultants (7) predict future economic problems for octane upgrading facilities with Arthur D. Little Inc. (8) showing economic viability for future ether and isomerization process installation.

The majority (80%+) of the available isobutane for MTBE formation is produced in FCCU operations at conventional oil refineries (9) and this is the basis for the present study, to evaluate the economics of a low cost simple add-on process for providing additional octane barrels to the unleaded gasoline pool by etherification.

Process optimization in terms of feedstock conversion and overall energy consumption has led to improved processes such as the NeoChem process (10) where the chemical equilibrium in the MTBE producing reaction is continuously disturbed by removal of the MTBE by distillation. This process was not considered in the present study but has gained a reputation as being one of the more innovative ether processes. The process basis of this study was to produce C_4, C_5 and C_6 ethers from FCC derived olefins using a single pass fixed bed reactor system with minimal purification and low capital cost.

2. EXPERIMENTAL

2.1 Feedstock Preparation

2.1.1 Methyl Tertiary Butyl Ether (MTBE) Feedstock

C_4 catalytically cracked hydrocarbons, typical of an alkylation plant feedstock were obtained from a Canadian refinery. Capillary column gas chromatography was used to characterize the hydrocarbons.

2.1.2 Methyl Tertiary Amyl Ether (TAME) and Tertiary Hexyl Methyl Ether (THME) Feedstock

A light catalytically cracked gasoline blending component was obtained from the same Canadian refinery. The TAME and THME feedstocks were separated from the gasoline blending stream by an atmospheric fractional distillation using a 200-L Sarnia Mark IV Fractionator. The C_5 fraction boiling between 25-50°C was collected as the TAME feedstock and the 50-75°C fraction was taken as the C_6 or THME feedstock. Gas chromatography was also used to characterize the hydrocarbons present in both feedstocks.

2.1.3 Gasoline Blending Stocks

In order to evaluate the effects of the produced ethers on fuel quantity, barrel quantities of a regular and premium unleaded gasoline product were also supplied from the same source. Compositional analyses of both gasolines were performed by mass spectrometry.

2.2 Oxyfuel Reactor

2.2.1 Reactor Design

Figure 1 shows the design of the pilot plant oxyfuel reactor. The unit basically consists of a 50-100 psig nitrogen blanketed feed tank seated on a scale, a preheater, an electrically heated reactor, a product cooler, a back pressure controller and a product reservoir.

The mixed feeds (hydrocarbons and methanol) were pumped to the top of the reactor by the metering pump (P-2). Premixing of the alcohol and hydrocarbon was used for the production of the TAME and THME ethers. The methanol feed can be introduced separately to the top of the reactor tube by pump P-1. Due to the volatility of the C_4 hydrocarbons, this procedure was used for the production of MTBE. The reactor effluent flowed to a solid trap (V-3A), the cooler (C-3), a back pressure control valve (V-3) and out into the product reservoir (V-4). The weight of the feed was recorded at regular intervals to determine feed rate. The accumulated weight of the drained product was used to determine mass balance. Gas chromatographic compositional analyses of the feed and product were used to determine component balances.

2.2.2 **Reactor Control**

2.2.2.1 **Temperature**

The reactor was heated electrically and controlled by a "Thermo-Electric" controller. A three section cooling coil installed between the reactor tube and heating element maintained more precise control of the reactor temperature and regulated the exothermic reaction heat produced from the methoxylation reactions particularly during the production of MTBE. Three thermocouples, dividing the reactor into three dimensionally equal sections, gave the temperature profile of the reactor.

2.2.2.2 **Feed Rate**

The feed rate was controlled by a Waters Model 510 HLPC metering pump.

2.2.2.3 **Pressure**

The reactor pressure was controlled from the pressure recorder controller (PRC-3). The PRC is a pneumatic pressure detecting device which was connected at the outlet of the reactor. It senses the pressure and activates the signal to the pressure control valve to open or close the valve depending on the pressure setting on the PRC. The product reservoir pressure was maintained by the nitrogen blanket on the feed tank and the vent system, RV-3.

The unit was considered free from the leaks if the PRC showed a pressure drop of less than 1 psi per hour during static testing.

2.3 Catalyst

The same catalyst, Rexyn 101(H) marketed by Fisher Scientific and made by Ionac Chemical, New Jersey was used for the C_4, C_5 and C_6 methoxylation studies. The catalyst is a cation exchange resin of styrene and divinyl benzene into which sulphonic acid ionic groups have been introduced.

The catalyst bed was prepared by sieving the 16-50 mesh Rexyn resin to a particle size of 18-28 mesh (0.6 to 1.0 mm), then drying overnight at 70°C. 80 mL (63.7 g) of dried catalyst was then charged to a 100 mL reactor. After contact with methanol the catalyst expanded 20% producing a 100 mL reactor bed. Both the particle sizing and drying procedures were necessary to prevent bed plugging problems.

The 100 mL reactor bed prepared in this manner was used for all 24 C_5 and C_6 reactor optimization experiments without a noticeable loss in reactivity.

2.4 Ether Process Optimization

2.4.1 C_4 (MTBE) Process Optimization

No process optimization studies of MTBE production were carried out. A literature search of some patents (11,12,13,14,15,16,17,18) pertaining to single pass cationic ion exchange resin fixed bed reactors indicated 75-85% conversion of isobutene to MTBE was possible from a catalytically cracked C_4 hydrocarbon stream using a reactor temperature of 50-125°C, a methanol/active C_4 molar ratio of 1 to 1.5 and a $LHSV^{-h}$ of 0.1 to 5.

The literature process conditions chosen for this study were as follows:

Reactor Temperature	= 100°C
$LHSV^{-h}$	= 1.5
Reactor Pressure	= 2.7 mPa
Methanol/Active Olefin Molar Ratio	= 1.2/1

2.4.2 C_5 (TAME) Process Optimization

The following twelve C_5 reactor optimization experiments were carried out using the 100 mL reactor:

Run #	Reactor Temp. °C	LHSV^{-h}	Methanol/Active Olefin Molar Ratio	Reactor Pressure (mPa)
1	65	0.5	1.09/1	1.7
2	80	0.5	1.09/1	1.7
3	95	0.5	1.09/1	1.7
4	65	2.0	1.09/1	1.7
5	80	2.0	1.09/1	1.7
6	95	2.0	1.09/1	1.7
7	65	0.5	0.74/1	1.7
8	80	0.5	0.74/1	1.7
9	95	0.5	0.74/1	1.7
10	65	2.0	0.74/1	1.7
11	80	2.0	0.74/1	1.7
12	95	2.0	0.74/1	1.7

Total mass balances were calculated from the recorded feed and product weights. Component balances based on the TAME reactive olefins and methanol consumption were calculated from the gas chromatographic compositional data.

Nitrogen and sulfur content were measured instrumentally with an Antek nitrogen and a Dohrman Microcoulometer analyzer, respectively. Oxygen content was calculated from the compositional data.

2.4.3 C_6 (THME) Process Optimization

The following twelve C_6 reactor optimization experiments were carried out using the same 100 mL reactor:

Run #	Reactor Temp. °C	LHSV^{-h}	Methanol/Active Olefin Molar Ratio	Reactor Pressure (mPa)
1	65	0.5	1.04/1	1.7
2	80	0.5	1.04/1	1.7
3	95	0.5	1.04/1	1.7
4	65	2.0	1.04/1	1.7
5	80	2.0	1.04/1	1.7
6	95	2.0	1.04/1	1.7
7	65	0.5	0.77/1	1.7
8	80	0.5	0.77/1	1.7
9	95	0.5	0.77/1	1.7
10	65	2.0	0.77/1	1.7
11	80	2.0	0.77/1	1.7
12	95	2.0	0.77/1	1.7

The elemental analyses, mass and component balancing techniques used for the C_5 optimization study were essentially duplicated for the C_6 study.

2.5 Ether Production Runs

Approximately 75 L of the C_4, C_5 and C_6 feed streams were separately methoxylated using a 1000 mL reactor under the following conditions:

	Reactor Temp. °C	LHSV^{-h}	Methanol/Active Olefin Molar Ratio	Reactor Pressure (mPa)
C_4 (MTBE) Ether	100	1.5	1.18/1	2.7
C_5 (TAME) Ether	65	0.5	1.04/1	1.7
C_6 (THME) Ether	80	0.5	0.99/1	1.7

The reactor products were stored at -20°C in stainless steel barrels and 10 mg/L Ethyl Corp. Agent 733 antioxidant was added to prevent gum and peroxide formation.

2.6 Process Purification of Ether Products

The following four techniques for the removal of unreacted hydrocarbon and methanol from the ether reaction products were investigated:

1) continuous recycle
2) glycol extraction
3) distillation
4) molecular sieve adsorption

2.6.1 **Continuous Reactor Recycle**

C_5 and C_6 product were separately recycled through the reactor using optimum conversion conditions (Section 2.5). Due to the reactor design and volatility of the C_4 hydrocarbons, the MTBE product was not recycled.

2.6.2 **Glycol Extraction**

C_5, C_5 and C_6 reactor products were separately placed in steel sample bombs and contacted with 0.5, 0.25 and 0.125 moles of glycol per mole of reactor product for 12 hours and then allowed to settle for 2 hours. Methanol contents were measured by gas chromatography.

2.6.3 **Distillation**

C_4, C_5 and C_6 reactor products were distilled using a 10 theoretical plate atmospheric fractionator. Distillation fractions were collected according to methanol, MTBE, TAME and THME boiling points and analyzed by gas chromatography.

2.6.4 **Molecular Sieve Adsorption**

C_4, C_5 and C_6 reactor products were separately passed through fresh molecular sieve beds under the following conditions:

Sieve type		= 4a (40-60 mesh)
Adsorber dimensions:	height	= 25 cm
	diameter	= 0.8 cm
	volume	= 12.56 cm^3
Weight of sieve		= 11.09 g
Flow rate		= 0.32 cm^3/min
Contact time		= 39.3 min
Temperature		= 23°C

Molecular sieve effluent fractions were analyzed for methanol until the adsorber showed no further affinity for alcohol removal.

2.7 Effect of Ether Compounds on Gasoline Quality

C_4, C_5 and C_6 methoxylation products, partially purified and totally purified ethers (by distillation) were blended according to total oxygen content into regular and premium unleaded gasoline. Each blend was monitored for research octane, motor octane, Reid vapour pressure and phase separation temperature. The details of the blending volumetrics are given in Table 1 and show the relationship between %, by volume oxygenate i.e. Methanol, MTBE etc. and % by weight, oxygen. Full C_6 methoxylation product blending was not possible due to the low THME yield.

In order to protect the blended fuels against phase separation, sufficient IPA cosolvent was added to equal the analyzed volume of methanol. The IPA oxygen content was included in the calculated oxygen value. Aromatic and water contents were also measured on the blending components to safeguard against unusual phase separation temperature phenomena.

2.8 Comparison of Ether Production Processes

Computerized linear program silulation involving a typical Canadian refinery was used to economically assess the value of the produced ethers as octane enhancers for gasoline.

Ether process test cases examined were as follows:

1) Base Case No. 1 - EMR Hycarb Report (1)
   Details of the Base Case input are given in the appendix of this report.

2) Study Case No. 1
   C_4 olefins to MTBE, unreacted C_4 olefins to alkylation
   C_5 olefins remain in FCC gasoline
   Lead and MMT allowed

3) Study Case No. 2
   C_4 olefins to alkylation
   C_5 olefins to TAME production
   Lead and MMT allowed

4) Study Case No. 3
   C_4 olefins to MTBE, unreacted olefins to alkylation
   C_5 olefins separately to TAME production
   Lead and MMT allowed

5) Base Case No. 2 (Hycarb Future Predictions)
   C_4 olefins to alkylation
   C_5 olefins remain in FCC gasoline
   LSR naphtha to isomerization
   No lead or MMT allowed

6) Study Case No. 4 (Hycarb Future Predictions)
   C_4 olefins to MTBE, unreacted C_4 olefins to alkylation
   C_5 olefins remain in FCC gasoline
   LSR naphtha to isomerization
   No lead or MMT allowed

7) Study Case No. 5 (Hycarb Future Predictions)
   C_4 olefins to alkylation
   C_5 olefins to TAME production
   LSR naphtha to isomerization
   No lead or MMT allowed

8) Study Case No. 6 (Hycarb Future Predictions)
   C_4 olefins to MTBE, unreacted olefins to alkylation
   C_5 olefins separately to TAME production
   LSR naphtha to isomerization
   No lead or MMT allowed

For study cases 5, 6, 7 and 8 where no lead or MMT was allowed, the extremely low octane quality light straight run naphtha (Deisohexanizer Overheads) was allowed back into the total gasoline pool by octane upgrading with an isomerization process. In an effort to remain consistent with the EMR forecasts, the Hycarb isomerization process input data was used. Details of the isomerization unit input data is given in the appendix.

3. RESULTS AND DISCUSSION

3.1 Methyl Tertiary Butyl Ether (MTBE)

3.1.1 Process Description

MTBE can be produced from the liquid phase exothermic reaction of isobutene and methanol at mild temperature and pressure conditions over a cationic exchange resin catalyst.

The chemical reaction involved is as follows:

$$\begin{matrix} CH_3 \\ | \\ C \\ | \\ CH_3 \end{matrix} = CH_2 + CH_3OH \underset{K_2}{\overset{K_1}{\rightleftharpoons}} CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-O-CH_3$$

Isobutene	+ Methanol	MTBE
m.w. = 56.1	m.w. = 32.0	m.w. = 88.1

The equilibrium reaction is reversible and the rate constants, K_1 and K_2 are both temperature dependent. However, the reverse reaction rate K_2 increases much more rapidly with temperature rise than does the forward reaction rate K_1. Therefore higher reactor temperatures will increase the reaction rate, but lower the isobutene conversion (9,19). Under the chosen process parameters, the isobutene reaction selectivity is near 100%, although at higher reactor temperatures and low methanol/isobutene molar ratios, some di and triisobutene can be produced.

About 85% of the North American supply of isobutene is found in refinery catalytic cracking mixed butene streams (10). However, as the mixed butenes comprise only 10-20% of the FCC reactor product and the isobutene content represents 9-17% of the mixed butene content, MTBE product costs and energy consumption can be uneconomically high. Variation in the mixed butene and related isobutene content is dependent upon such variables as FCC design, feed quality, operation severity and catalyst type.

The design of the MTBE process shown in Figure 2 is for the methoxylation of up to 700 m^3/d C_4 FCC feed stream before the presentation of this feedstock to an alkylation or poly gas plant.

As the methoxylation process removes only the 9-17% isobutene content from the FCCU-C_4 stream by reacting it with methanol to form MTBE, much of the process involves the removal of methanol and ether from the unreacted C_4, since both alkylation and poly gas catalysts are adversely affected by moisture and related compounds.

Strong acid alkylation (HF or H_2SO_4) or poly gas (P_2O_5) catalysts will react with alcohols to form salts and water.

$$HX + ROH \longrightarrow RX + H_2O$$

Such reactions of methanol, remaining with the unreactable C_4 in the effluent stream from the oxygas reactor, are detrimental to an alkylation since both catalyst is consumed and water is produced. Both of these aspects are especially important in HF alkylation where the HF is expensive and the presence of any water leads to severe corrosion problems. In fact, molecular sieve or alumina dehydrators are standard equipment for trace water removal in HF alkylation reactors. The maximum water content in feed to HF alkylation units is 5 ppm, w/w. The water tolerance for H_2SO_4 alkylation is not as severe because H_2SO_4 is less expensive and less corrosive. Typically there is water washing upstream of H_2SO_4 alkylation units and therefore the C_4 hydrocarbon feed is saturated with water i.e. 100 ppm w/w H_2O. Polygas catalyst water tolerance appears to be somewhere in between the two alkylation catalysts, approximately 80 ppm w/w H_2O.

In order to assess the economics of oxygasoline processing in comparison with alkylation, the value of isobutene as a feed for these two competing processes must be considered. There are some conflicting results in the literature for HF alkylation where the order of butenes in descending octane importance are:

2-butenes>isobutene>1-butene (20,21) or isobutene>2-butenes> 1-butene (22). According to Albright (23), isobutene is the least desirable feed for H_2SO_4 alkylation and the ranking is as follows: 2-butenes>1-butene>isobutene.

Thus with consideration to both water tolerance and isobutene content, a MTBE plant can be more economically interfaced with H_2SO_4 alkylation rather than a HF unit.

However, the removal of methanol and ether from unreacted C_4 hydrocarbons is still of paramount importance and is responsible for the major portion of the estimated MTBE process capital cost.

Removal of methanol and ethers from unreacted hydrocarbons by distillation is quite complicated as both methanol and water form azeotropes with MTBE and methanol forms azeotropes with most or all the C_4 present. If C_4 and C_5 FCCU streams were simultaneously methoxylated in the same reactor, the additional TAME azeotropes could place sufficient economic stress upon the necessary unreacted C_4 hydrocarbon separation as to render this single fixed bed reactor concept as impractical.

Pressurized azeotropic distillation (24,25,26) coupled with water extraction is used for the separation of MTBE, unreacted C_4 hydrocarbon and methanol. Molecular sieve adsorption (6) and glycol extraction (27) also have application for removal of methanol from C_4 hydrocarbons.

Included in the MTBE plant cost estimate for the processing of up to 700 m^3/d C_4 FCC feedstock is a reactor, a distillation tower to separate MTBE from C_4 hydrocarbon and methanol and a glycol extraction and associated stripping column for the separation of unreacted methanol from the C_4 hydrocarbons (28). The glycol processing will satisfy the ppm methanol restriction for a C_4 alkylation feedstock, and the distillation tower will produce a technical grade of MTBE (97-99%) suitable for gasoline blending.

3.1.2 Process Data

A literature search of some patents (11,12,13,14,15,16,17,18) pertaining to single cationic ion exchange resin fixed bed reactors indicated 75-85% conversion of isobutene to MTBE was possible from a FCCU C_4 stream using a reactor temperature of 50-125°C, a methanol/active C_4 molar ratio of 1 to 1.5 and a $LHSV^{-1}$ of 0.1 to 5.

The literature process conditions chosen for this pilot plant study were as follows:

Reactor Temperature	= 100°C
LHSV^{-h}	= 1.5
Reactor Pressure	= 2.7 MPa
Methanol/Active Olefin Molar Ratio	= 1.2/1

Based upon these process conditions and a C_4 alkylation unit feed (Table 2) containing 10.24% 1/v isobutene, an overall active C_4 olefin conversion of 80.0% (Table 3) was obtained.

The 80.0% averaged isobutene to MTBE conversion value is based upon the following two methods of calculation and the assumption that the isobutene to MTBE reaction was 100% specific for these process parameters:

(i) The amount of unreacted isobutene remaining in the product as compared to isobutene feed content (82.0% conversion).

(ii) The stoichiometric amount of isobutene necessary to produce the amount of MTBE found in the product as compared to isobutene feed content (78.0% conversion).

The grams per hour (g/h) in Table 3 relate to a 1000 mL reactor and show only the components involved in reaction i.e. such components as 12.8% trans-2-butene or 4.44% isopentane (Table 2) are not shown.

Difficulties were encountered in closing 100% total mass and component balances for isobutene and methanol. It is believed that the mass and component balancing was affected by the fact that the volume of unreacted C_4 hydrocarbons contained in the off-gas was measured by a wet test meter and the weight of unreacted hydrocarbon was calculated from a mass spectrometer analysis. Additional losses in methanol content also probably resulted from phase separation of methanol caused by water extraction. Water is produced by a methanol-dimethyl ether side reaction.

$$2\ CH_3OH \longrightarrow CH_3OCH_3 + H_2O$$

Methanol	Dimethyl Ether	Water
m.w. = 32	m.w. = 46	m.w. = 18

Table 4 gives the detailed compositional analysis of the reactor feed, the final product and the unreacted C_4 off-gas.

Under the chosen conditions of 100°C, 2.7 mPa, $LHSV^{-h}$ = 1.5 and a methanol/active olefin molar ratio of 1.2, the 80% isobutene conversion shows good agreement with literature values (11,12,13, 14,15,16,17,18). The selectivity of isobutene to form MTBE may be considered as approaching 100% under the process conditions studied. The selectivity of methanol to form MTBE is less than 100%, the dimethyl ether side reaction does occur and is aggravated by higher reactor temperatures. The linear program input data takes into consideration additional methanol consumption due to the less than 100% selectivity of methanol to form MTBE.

Although no noticeable loss in catalyst activity was observed, a once-a-year change of the cationic exchange resin has been included in the operating costs for the linear program. Excessive heat or alkali will damage this catalyst.

3.1.3 Separation of Methanol, MTBE and Hydrocarbons for Product Evaluation

Distillation data given in Table 5 demonstrates that methanol and MTBE cannot be adequately separated from unreacted C_4 hydrocarbon with a conventional atmospheric distillation. As previously discussed, pressurized azeotropic distillation coupled with water extraction is necessary to purify MTBE and separate trace methanol (ppm level) from unreacted C_4 hydrocarbon.

Table 5 also demonstrates the affinity of both glycol and molecular sieves for methanol; however, both techniques are generally used only for the separation of unreacted methanol from C_4 hydrocarbon following the distillation removal of MTBE.

3.1.4 MTBE Product Quality Assessment

3.1.4.1 Blending Octane Values - Precision

Blending octane numbers were determined on blends of oxygenates in both premium and regular unleaded gasolines in the range of 0-6% oxygen by weight. In this study, only single octane number

determinations were made by both the Research ON method (ASTM D2699) and Motor ON method (ASTM D2700) which have the following quoted test reproducibility:

Research ON	(ASTM D2699)	0.7 (for 90-100 RON range)
Motor ON	(ASTM D2700)	1.1 (for 80-95 MON range)

Small recorded differences in determined octane numbers may be inside test reproducibility and they can have significant effects on apparent blending octane number.

3.1.4.2 **Blending RVP for n-Butane**

An important consideration in gasoline blending, when utilizing oxygenates, is the effect on backing out or backing in n-butane while maintaining a specific RVP.

The effect on RVP of blending n-butane into gasoline has been established for a debutanized gasoline basestock with calculated butane additions. Figure 3 shows this calculated theoretical relationship which was used to estimate the n-butane back in or back out resulting from blending the various oxygenates while maintaining the original blend RVP.

3.1.4.3 **Methanol-Gasoline Base Case Blends**

Blends of premium and regular unleaded gasolines with three methanol/isopropanol mixtures were prepared at a constant 4% combined oxygen content. The data is given in Tables 6 and 7 and shows that:

a) Methanol exhibits a high blending Research ON of about 124 (Figures 4 and 5).
b) Methanol exhibits a much lower blending Motor ON of about 99 in premium gasoline and only about 94 in regular gasoline (Figures 4 and 5).
c) There is a serious negative effect on RVP leading to a loss of up to about 5% vol butane (Figures 3, 6 and 7) to maintain RVP.
d) The front end distillation characteristics as measured by 10% evaporated temperature is significantly depressed (Tables 6 and 7).

The results are comparable to published data (1) and demonstrate the serious economic penalty on refinery butane disposal opportunities and the need to use expensive cosolvents such as C_3 and C_4 alcohols to avoid phase separation at low temperatures.

3.1.4.4 MTBE - Gasoline Blends

From the data given in Tables 8 and 9, MTBE demonstrates an average apparent blending octane number of about 116 Research ON and 101 Motor ON in both the premium and regular unleaded gasolines. The actual blending octane number varies with the basestock ON and oxygenate concentration level as shown in Figures 8 and 9. The results obtained in this study agree closely with literature values (3,19).

Blending MTBE in either premium or regular unleaded gasolines at up to 26% vol (6% wt oxygen), which is well above the 11% vol allowed by EPA, did not abnormally disturb the volatility of the blends in terms of either RVP or ASTM D86 distillation which is a marked contrast to use of methanol (Figures 10 and 11). To safeguard against any unusual gasoline formulation, a 15% by volume maximum distillation blending restriction was placed on the MTBE linear program product quality input data. Data shown in Table 10 and derived from Figure 3 demonstrates that use of 5-10% vol MTBE as an octane improver in unleaded gasoline would allow about 1% volume additional n-butane to be added to maintain the original blend RVP. This 1.0% additional n-butane value was used in the MTBE linear program product quality input data. Additional butane disposal opportunities offer economic advantage for both gasoline processing costs and octane enhancement.

MTBE improves both gasoline octane number and volatility in a comparable way to toluene and in fact the economics of MTBE have been shown to offer some alternative to toluene production through high severity reforming (3).

Extensive commercial use of MTBE has demonstrated no problems with phase separation at low temperatures. Phase separation temperatures shown in Tables 8 and 9 were negatively affected by several factors, i.e. the high water content of the base fuels and the MTBE used, the aromatic content of the base fuels and the blended oxygenate levels. Hydrocarbon and water content of all blending components are shown in Table 11.

3.1.5 MTBE Linear Program Input Data

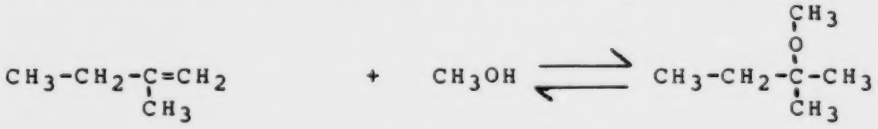
Input data derived from the MTBE process and product evaluation studies (3.1.2, 3.1.4) was used in a computerized simulated linear program model of a typical Canadian refinery in order to assess the economic viability of an integrated C_4 ether process in a refining environment. Details of the MTBE computer input and product quality data is given in the appendix.

3.2 Tertiary Amyl Methyl Ether (TAME) Process and Product Evaluation

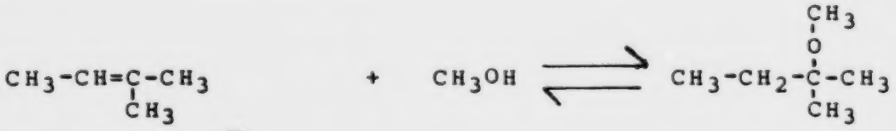
3.2.1 Process Description

TAME can be produced from the exothermic liquid phase reaction of 2-methyl-1-butene and/or 2-methyl-2-butene with methanol at mild temperature and pressure conditions over the same cationic exchange resin catalyst used to produce MTBE.

The chemical reactions involved are as follows:



2-Methyl-1-Butene	Methanol	Tertiary Amyl Methyl Ether
m.w.=70.1	m.w.=32.0	m.w.=102.1



2-Methyl-2-Butene	+	Methanol	Tertiary Amyl Methyl Ether
m.w.=70.1		m.w.=32.0	m.w.=102.1

The equilibrium reaction is clearly reversible throughout the temperature range of interest. A reactor temperature rise favours the reverse reaction, but increases the reaction rate. The equilibrium conversion for the TAME reaction does not favour ether formation as much as it does in MTBE formation from isobutene and

methanol. However, the selectivity of the C_5 reaction of TAME is better than isobutene to MTBE, due to the lack of diisoamylene formation (29).

The installed cost of the TAME process shown in Figure 12 is estimated at $500,000 and is designed to be integrated into a refining environment and process 480 m^3/d of FCC C_5 hydrocarbons. This cost does assume a methanol feed tank and transfer system are already on-site. Presently Lindsey Oil, UK are scheduled to bring on line this year, a TAME facility to process 875 m^3/d of C_5 FCC gasoline (19). This plant will be the first reported plant to exclusively process a C_5 FCC feedstock in an integrated refining environment.

As process conversion and octane quality of TAME are both lower than MTBE and the mixed C_5 feed comprises only 8-14% of the FCC reactor product of which 10-20% is active C_5 hydrocarbon, many refiners feel that FCCU produced TAME would not significantly increase the clear octane quality of their gasoline pool.

The ether processing of the C_5 FCC gasoline has been made independent of the C_4 and C_6 FCC feedstocks in this study due to the separation difficulties involved with methanol and C_4 hydrocarbons and the relatively low octane quality of the C_6 ethers.

Unlike the C_4 ether process, the unreacted C_5 hydrocarbons do not go on for further processing. By using less than a stoichiometric amount of methanol feed, a C_5 reactor product having a sufficiently low methanol content can be produced so as to be directly suitable for gasoline blending purposes. The elimination of an alcohol removal system greatly reduces both the capital and operating costs for the manufacture of the C_5 ether.

As most refineries have distillation facilities to separate LCC gasoline (basically C_5 and C_6 hydrocarbons) and HCC gasoline (C_7-C_{10} hydrocarbons), no additional cost was allocated for preparation of the C_5 ether feedstock. It is proposed to optmize the FCC gasoline distillation tower so as to bring the C_5 fraction overhead while leaving the C_6 fraction in the HCC gasoline blending stream.

3.2.2 TAME Process Data

A 25-50°C C_5 FCC feedstock was prepared by distillation from a LCC gasoline blending stock. The feedstock compositional data given in Table 12 shows the presence of 43.5% isopentane, 15.3% active C_5 olefins and 1.33% active C_6 olefins.

The 15.3% active C_5 olefin content is comprised of 4.7% 2-methyl-1-butene (B.P.=31.2°C) and 10.6% 2-methyl-2-butene (B.P.=38.6°C). The C_5 active olefin content could have been further concentrated by removing most of the 43.5% isopentane (B.P.=27.9°C) by collecting the distilled fraction boiling between 29-50°C, instead of 25-50°C. However, the removal of the isopentane would cause a substantial reduction in 2-methyl-1-butene, which appears to have a much greater tendency to form TAME than the 2-methyl-2-butene isomer. If a depentanized C_5 feed were used, i.e. 29-50°C fraction, a smaller reactor would be required; however, the isoamylene-ether conversion would drop significantly (28).

Twelve C_5 reactor optimization experiments (Tables 13, 14, 15 and 16) varying the reactor temperature, LHSV and methanol/active olefin molar ratio were carried out using a 100 mL reactor. The experimental details are given in Section 2.4.2.

The g/h results given in Tables 13, 14, 15 and 16 relate to the 100 mL reactor and show only the components involved in reaction, i.e. 43.5% isopentane is not shown.

Gravimetric mass balancing of the feed and reactor product ranged from 95.1 to 100.0% for the twelve experiments. These results indicate the reactor system was virtually leak free.

Component balancing based upon unreacted and TAME-reacted isoamylene ranged from 99.5 to 105.7%. These results indicate the isoamylene-TAME reaction is virtually a 100% specific under the process condition studied. Conversion of isobutene to MTBE has been reported as <100% specific for methanol/active olefin molar ratios of <1 (30). This data shows isoamylene conversion to TAME has remained 100% specific even at feed ratios of 0.74 moles of methanol to 1 mole of active olefins.

The selectivity of the methanol reaction to TAME decreases with temperature increase, largely due to dimethyl ether formation (see

Section 3.1.2). Other than dimethyl ether, no other methanol by-product was detected. Examination of the mass balance data based upon total methanol consumption shows considerable deviation from 100% (85.3 to 110.0%). This mass balance variation is believed to be largely due to the following analytical difficulties:

1) As dimethyl ether has a boiling point of -25°C, reactor dispensing and analytical transfer difficulties were encountered.

2) At higher temperatures, sufficient water was generated from the dimethyl ether reaction to extract methanol from the product leaving a two-phase system. Sec-butyl alcohol was used to restore the reactor products to a one-phase system for Runs 4 to 12. Runs 1, 2 and 3 reflect a lower methanol consumption balance due to the absence of the sec-butyl alcohol cosolvent.

Isoamylene conversions are based upon the g/h active C_5 entering the reactor and the g/h unreacted isoamylene found in the product effluent.

Conversion values based upon 2-methyl-1-butene and 2-methyl-2-butene do not take into considerabion the isomerization of 2-methyl-1-butene to 2-methyl-2-butene. The results have been expressed in this manner to demonstrate the increased tendency of 2-methyl-1-butene to either isomerize or form TAME.

Comparison of feed nitrogen and sulfur levels with the twelve product effluents shows a considerable reduction in most cases. However, no catalyst deactivation was apparent.

Oxygen values have been calculated from the compositional data and include all unreacted methanol and oxygenate products produced, i.e. MTBE, TAME, THME and Dimethyl Ether.

3.2.3 **Selection of TAME Process Conditions**

Based upon the twelve C_5 optimization experiments carried out, the most suitable operating conditions for the production of TAME from a C_5 FCC gasoline are (Run 1):

Reactor Temperature	= 80°C
$LHSV^{-h}$	= 2.0
Reactor Pressure	= 1.7 mPa
Methanol/Active Olefin Molar Ratios	= 0.74/1

The reasons for this selection were as follows:

1) Reactor Temperature

Examination of the influence of reactor temperature upon C_5 ether production carried out in this study confirms the literature references (19,29) and indicates the methoxylation of active C_5 is an equilibrium-controlled reversible reaction with the conversion to TAME decreasing with temperature and the rate of reaction increasing with temperature. With regard to this criteria, 80°C was the optimum reactor temperature recorded in this study.

2) $LHSV^{-h}$

A maximum isoamylene-TAME conversion of 58.8% was obtained for a $LHSV^{-h}$ of 0.5, which probably approaches the equilibrium conversion for stoichiometric or slightly above stoichiometric methanol with isoamylene. However, a 0.5 $LHSV^{-h}$ would necessitate an unreasonable large reactor. Based upon the experimental data generated in this study, a space velocity of 2.0 is the most suitable processing condition.

3) Reactor Pressure

1.7 mPa is sufficient pressure to ensure the methoxylation reaction takes place in the liquid phase.

4) Methanol/Active Olefin Molar Ratio

Data given in Table 17 shows that a reduction of methanol/active olefin molar ratio from 1.1 to 0.74 reduces conversion from 50.6% to 43.5%. However, 2.8% unwanted methanol would remain in the reactor product as compared to 1.2% for the less than stoichiometric 0.74/1 molar feed ratio. A 1.2% C_5 reactor product methanol content is considered to be suitable for direct gasoline blending in amounts up to 20% i.e. the resultant 0.24 methanol content in the final gasoline product would provide additional fuel line freezing protection properties. A 20% blend of the 2.8% methanol content C_5 reactor effluent would produce a marginal to unacceptable product, depending upon the marketing region. The 0.74/1 methanol/active olefin

molar ratio has been chosen as the most desirable feed ratio as only a 7.1% loss in conversion was recorded while 4.0 m^3/d less methanol could be purchased and no relatively expensive methanol removal system was required.

3.2.4 Preparation of TAME for Product Quality Assessment

The process conditions chosen to produce sufficient TAME for product quality assessment were:

Reactor Temperature	= 65°C
$LHSV^{-h}$	= 0.5
Reactor Pressure	= 1.7 mPa
Methanol/Active Olefin Molar Radio	= 1.1/1

Although these operating parameters are in contradiction to the process conditions selected in Section 3.2.3, the above selection (Run 1, Table 13) maximized the TAME product content. Due to the insensitivity of some of the more significant gasoline product quality tests, maximum TAME product content was believed important.

The g/h results given in Table 18 relate to a 1000 mL product reactor rather than a 100 mL optimization reactor. The data shows good isoamylene-TAME conversion agreement for this tenfold expansion in reactor size i.e. for the 100 mL reactor the conversion was 58.8%, while the 1000 mL reactor showed a 60.8% conversion.

The method of calculation and recording of results is identical to the C_5 optimization experiments with the exception that periodic feed and product samples were taken to ensure uniform processing.

Table 19 shows the complete composition by volume of the C_5 reactor feed and composite final product. This data differs from the Table 18 g/h results which displays only the components involved in the reaction.

3.2.5 Separation of Methanol, TAME and Unreacted Hydrocarbons for Product Evaluation

Data given in Table 20 shows that a technical grade of TAME suitable for gasoline blending can be distilled from unreacted methanol

and hydrocarbon. Some of the TAME used in the product evaluation blending studies was prepared by distillation.

Table 20 also demonstrates the affinity of both glycol and molecular sieves for methanol in the presence of unreacted hydrocarbon and TAME.

Table 21 shows that unreacted methanol cannot be satisfactorily removed by recycling of reactor product. As previously mentioned, a maximum 58.8% equilibrium conversion for a $LHSV^{-h}=0.5$ and 1.1/1 methanol/active olefin ratio was obtained. This data shows a 27.5% conversion on the recycled product was obtained for a 0.7/1 methanol/active olefin ratio. The recycle operating parameters are almost identical to those used in the C_5 optimization Run 7 (Table 15) where a 53.1% conversion was obtained.

The overall conversion of the recycled product is 56.3% and generally agrees with the expected 58.8% maximum equilibrium conversion. This 56.3% conversion is based upon the 4.71 g/h isoamylene contained in the original C_5 FCC feed and the 2.06 g/h isoamylene remaining in the recycled product.

3.2.6 TAME Product Quality Assessment

3.2.6.1 Blending Options Examined

TAME was evaluated in three modes as follows:

(a) purified TAME
(b) a 50% by volume purified TAME
(c) as C_5 reactor effluent from the etherification process

A major objective was to octane upgrade the quality of the C_5 fraction from FCC gasoline as a fuel component with minimum processing and purification. A second objective was to study the impact of unreacted methanol remaining in the C_5 TAME reactor effluent on gasoline product quality.

3.2.6.2 Blending Octane Number and Volatility of TAME and C_5 Reactor Effluent

Blends of pure TAME C_5 reactor effluent and partially purified TAME (50% TAME) in both premium and regular unleaded gasolines were prepared in the range of 0-3% wt combined oxygen and the data are given in Tables 22, 23, 24, 25, 26 and 27 and displayed in Figures 13, 14, 15, 16, 17 and 18.

The average blending Research ON for TAME was 106 RON and the average blending Motor ON was 99 (Figures 13, 14). These are both lower than the blending octane values for MTBE but compare favourably with published values (19,28).

The effect on gasoline volatility of blending pure TAME into either premium or regular gasoline, is similar to that found for MTBE (Figures 19 and 20). The data given in Tables 22 and 23 and Figures 21 and 22 shows that at least 25% vol TAME can be incorporated into either normal winter or summer gasolines without creating specification violations. Data shown in Table 28 and derived from Figure 3 shows that at a level of 10% vol TAME in unleaded gasoline, an additional 1% vol n-butane can be incorporated to maintain original blend RVP.

For the C_5 reactor effluent, the blending octane values for the 43.5% vol isoamylene to TAME conversion were arrived at by calculation from all the available data. The calculation is shown in the appendix. The C_5 feedstock octane numbers were determined to be 95.3 RON and 84.0 MON while the calculated C_5 reactor effluent (43.5% conversion) was 96.3 RON and 85.8 MON for the process conditions given in Section 3.2.3. Those octane blending values were used in the linear program product quality input data for C_5 reactor effluent. At this conversion level, which results in the minimum unreacted methanol remaining in the product, there is an octane improvement of 1 RON and 1.8 MON over the feedstock. Thus the simple upgrading of the C_5 stream from FCCU gasoline by etherification, can produce a useful octane improvement without costly additional downstream processing/separation stages or use of expensive cosolvents to correct phase separation problems arising from unreacted methanol in the effluent.

The C_5 reactor effluent contains unreacted hydrocarbons, TAME and some methanol and is a relatively volatile stream. The data in Tables 24 and 25 and Figures 23 and 24 show that up to 25% vol C_5 reactor effluent can be blended into normal summer and winter grade gasolines without causing distillation specification violations. The C_5 reactor effluent has been assigned an approximate approximate 1.5% back out of n-butane to maintain original blend RVP (Figures 25 and 26) as the unleaded premium and regular gasolines used in this study were refinery formulated with FCCU gasolines already containing the volatile C_5 fraction.The 1.5% n-butane back out used in the TAME reactor effluent linear program input data is attributed to the unreacted methanol remaining in the ether blending stock.

3.2.7 Linear Program Input for TAME

Input data derived from the TAME process and product evaluation studies (3.2.2, 3.2.3, 3.2.6) was used in a computerized simulated linear program model of a typical Canadian refinery in order to assess the economic viability of an integrated C_5 ether process in a refining environment. Details of the TAME process and product quality input data are given in the Appendix.

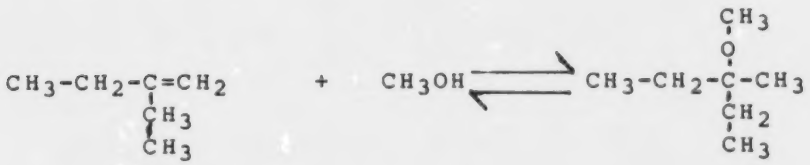
3.3 Tertiary Hexyl Methyl Ether (THME) Process and Product Evaluation

3.3.1 Methoxylation of a C_6 FCCU Feedstock

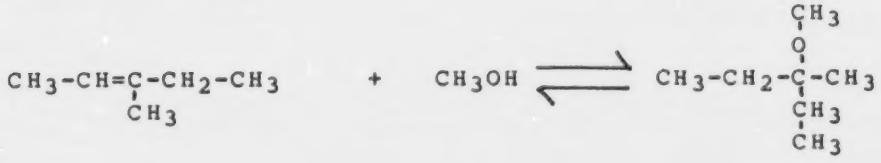
Four THMEs can be produced from eight active C_6 olefins in a liquid phase reaction with methanol at mild temperature and pressure over the same REXYN 101(H) cationic exchange resin used to produce the C_4 and C_5 ethers.

The chemical reactions involved are as follows:

1) 3-Methyl-3-Methoxy Pentane from 2-Ethyl Butene-1 and Cis and Trans-3-Methyl Pentene-2

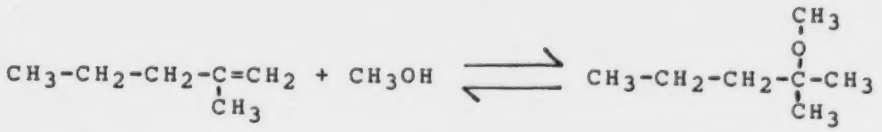


2-Ethyl Butene-1 m.w.=84.2 | Methanol m.w.=32.0 | 3-Methyl-3-Methoxy Pentane m.w.=116.2

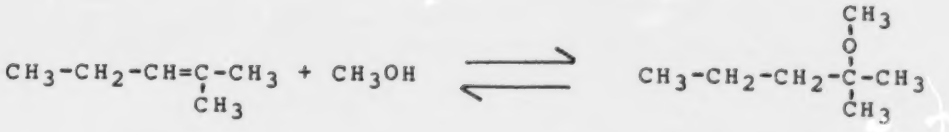


Cis & Trans 3-Methyl Pentene-2 m.w.=84.2 | Methanol m.s.=32.0 | 3-Methyl-3-Methoxy Pentane m.w.=116.2

2) 2-Methyl-2-Methoxy Pentane from 2-Methyl Pentene-2 and 1-Methyl Pentene-2

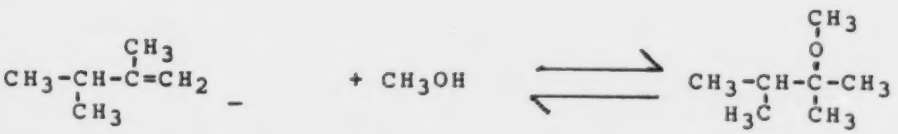


2-Methyl Pentene-1 m.w.=84.2 | Methanol m.w.=32.0 | 2-Methyl-2-Methoxyl Pentane m.w.=116.2



2-Methyl Pentene-2 m.w.=84.2 | Methanol m.w.=32.0 | 2-Methyl-2-Methoxy Pentane m.w.=116.2

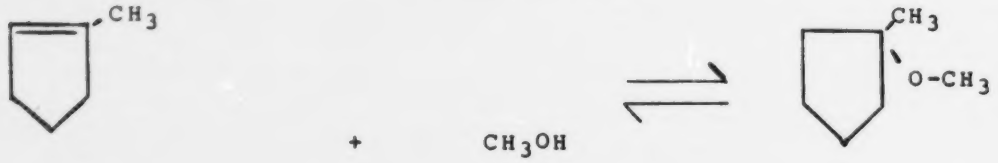
3) 2,3-Dimethyl-2-Methoxy Butane from 2,3-Dimethyl Butene-1 and 2,3-Dimethyl Butene-2



2,3-Dimethyl Butene-1 m.w.=84.2 | Methanol m.w.=32.0 | 1,3-Dimethyl-2-Methoxy Butane m.w.=116.2

2,3-Dimethyl Butene-2 m.w.=84.2 | Methanol m.w.=32.0 | 2,3-Dimethyl-2-Methoxy Butane m.w.=116.2

4) 1-Methyl-1-Methoxy Cyclopentane from 1-Methyl Cyclopentene-1



1-Methyl Cyclopentene-1 m.w.=82.1 | Methanol m.w.=32.0 | 1-Methyl-1-Methoxy Cyclopentane m.w.=114.1

3.3.2 THME Process Data

A 50-75°C C_6 FCC feedstock was prepared by distillation from a LCC gasoline blending stock. The feedstock compositional data given in Table 29 shows the presence of 0.97% active C_5 olefins and 11.8% active C_6 olefins.

The twelve optimization experiments shown in Tables 30 to 33 demonstrate the methoxylation of active C_6 olefins is similar to the C_5 reaction. That is, the C_6 reaction is reversible throughout the temperature range of interest with higher reactor temperatures giving lower conversions and more rapid reaction rates.

The g/h results relate to a 100 mL reactor and show only the components involved in reaction.

Gravimetric mass balancing of the feed and reactor product ranged from 97.5% to 100.9%, indicating the reaction system was virtually leak-free.

Component balancing based upon the total active C_6 olefin in and out of the reactor ranged from 93.9 to 114.2% indicating that the methoxylation of C_6 olefin is at least 93.9% specific.

Component balancing based upon methanol consumption ranged from 59.0 to 114.2% even with the use of isopropyl alcohol co-solvent. This data does suggest that methanol side reactions other than dimethyl ether formation could be occurring.

Isohexylene conversion to THME has been calculated by the following two techniques:

i) The amount of C_6 active olefin present in the feed as compared to the amount of C_6 olefin required to produce the volume of THME found in the reactor product.

ii) The amount of active C_6 olefin found in the feed as compared to the unreacted active C_6 olefin remaining in the product.

With the degree of analytical difficulty involved in separating the hydrocarbons of interest and the assumption that the isohexylene to THME reaction is 100% specific, agreement between the two conversion calculations is surprisingly good.

Although the eight individual C_6 active olefins and four C_6 ethers have been separately tabulated, no direct component balancing for lindividual THME isomers (see Section 3.3.1) has been attempted, due to olefin isomerization.

Comparison of the nitrogen and sulfur feed and product levels indicates in some cases sulfur was being released from the catalyst bed possibly related to the previous processing of C_5 olefins. No noticeable loss in catalyst activity was apparent.

Oxygen contents were again calculated from compositional data and include unreacted methanol and all oxygenates produced.

3.3.3 Selection of THME Process Conditions

The methoxylation of C_6 FCC olefins was not selected as an integrated petroleum refining octane enhancing process. The reasons are as follows:

1) Very little octane improvement was found. The eight C_6 active olefins and the four C_6 ether products all have similar octane blending characteristics (Table 42).

2) The FCC reactor product contains only 3-6% C_6 olefins of which 10-15% are ether reactive.

3) Based upon a single-pass fixed-bed reactor system, an isohexylene process conversion of only 30% would be expected.

3.3.4 Preparation of THME for Product Quality Assessment

The process conditions chosen to produce THME for product quality assessment were:

Reactor temperature	= 80°C
$LHSV^{-h}$	= 0.5
Reactor pressure	= 1.7 mPa
Methanol/Active Olefin Molar Ratio	= 1.1/1

These conditions gave an averaged maximum 41.3% conversion of ether-reactive C_6 olefins to THME. Due to the insensitivity of some of the more significant gasoline product tests and the low conversion rate, maximum THME product content was again believed important.

The g/h results given in Table 34 relate to a 1000 mL product reactor rather than the 100 mL optimization reactor.

The 38.2% overall averaged conversion based upon the 1000 mL reactor is in reasonable agreement with the anticipated 41.3% conversion obtained in the 100 mL optimization reactor.

Table 35 shows the complete composition by volume of the C_6 reactor feed and composite final product.

3.3.5 Separation of Methanol, THME and Unreacted Hydrocarbons for Product Evaluation

Data given in Table 36 shows that a technical grade of THME suitable for gasoline blending can be distilled from the unreacted methanol and hydrocarbon. A THME-distilled product having a

purity of 93.5% was used to establish the gasoline product quality of the C_6 ethers. However, due to the low ether reactive C_6 olefin content of the feed and the limited conversion, the quantity of THME produced did not allow for as complete a product evaluation as carried out for the C_5 ether.

Glycol extraction and molecular sieve adsorption data for methanol in the presence of THME and C_6 hydrocarbon is also given in Table 36.

Table 37 demonstrates that the C_6 methoxylation reaction is an equilibrium reversible reaction similar to the TAME reaction and methanol cannot be satisfactorily removed by a recycle operation.

The overall recycle conversions of 38.0% based upon a total active C_6 mass balance and 39.5% based upon the produced THME approaches the maximum equilibrium conversion conditions of 39.4 and 43.3% (Run #2, Table 30).

3.3.6 THME Product Quality Assessment

3.3.6.1 Blending Options Examined

THME was evaluated in the following modes:

a) purified THME
b) C_6 reactor effluent from the etherification process

As in the C_5 case (Section 3.2.6.1), the objective was to evaluate the upgrading of the C_6 fraction from FCC gasoline as a fuel component with minimum processing and purification.

3.3.6.2 Blending Characteristics of THME and C_6 Reactor Effluent

Data shown in Tables 38 to 41 and portrayed in Figures 27 to 30 shows that under the blending conditions used, THME did not produce improvements in octane quality. Octane data for the ether precursors (31) and for pure THME, C_6 reactor effluent, C_6 reactor feedstock and the unreacted C_6 hydrocarbons are given in Table 42. Published data (19) confirms the lack of octane improvement from C_6 ethers.

Addition of C_6 ethers to either the winter or summer grade gasolines caused reductions in Reid Vapour Pressure (Figures 31 to 34) and, as shown in Table 43, would allow up to an additional 1.5% L/v n-butane to be added to maintain overall blend RVP.

3.3.6.3 Phase Separation Characteristics of THME

Phase separation of oxyfuels is dependent on such variables as water content, aromaticity, presence of cosolvents, oxygenate concentration and temperature.

Data for the aromatic and water content of the base gasolines and ethers is given in Table 11.

3.4 Economic Evaluation of Ether Processes

A computerized simulated linear program model of a typical Canadian refinery was used to assess the economic viability of integrated C_4 and C_5 ether processes in a refining environment

Economic predictions given in Table 44 show the TAME process from Study Case No. 2 and the Base Case No. 2 (see Section 2.8 for definitions) as the only two study cases having economic advantage over the original refinery "as is" Base Case No. 1. Future forecasts as related to the Hycarb report (1) show a negative economic impact for both the C_4 and C_5 ether processes separately and collectively when compared to Base Case No. 2.

Based upon the Study Case No. 2 and Base Case No. 2 economic comparisons with Base Case No. 1, the $500,000 TAME plant in Study Case No. 2 had a return on investment (ROI) of about 4 years, while the $18,000,000 isomerization unit ROI was approximately 11 years using after tax dollars.

3.4.1 MTBE Economic Assessment

Surprisingly, the linear program under the proposed study conditions, continually denied the use of the C_4 ether process as an economic means of gasoline octane enhancement.

The major reason for this economic failure is due to the MTBE process being in octane competition with the alkylation process.

MTBE and alkylation comparison data given in Tables 45 and 46 shows MTBE as being both the smallest processed volume and octane-m^3 contributor to the total gasoline blending pool. An octane-m^3 is defined as the processed volume of the gasoline blending component times the calculated octane road index.

Table 45 shows in all study cases that when MTBE competes directly with alkylation for isobutene, a negative octane-m^3/year contribution ranging from 2.2 to 4.5 X 10^6 octane-m^3/year was obtained.

The explanation of this negative octane-m^3/year data is demonstrated in Table 47. Alkylation unit capacity is sized directly in relationship to the volume of FCC C_3 and C_4 olefins and octane quality is optimized by controlling the ratio of the FCC olefins and C_3 and C_4 paraffins derived from FCCU, crude units and outside purchase. Total alkylation feed (Table 47) when coupled with a MTBE plant is therefore reduced by approximately 20%, which results in a 20% under utilization of the 1000 m^3/stream day (SD) alkylation plant (Table 48). Table 49 reflects the subsequent 15-20% reduced field butane purchase which would have been utilized as alkylation feed if the MTBE plant had not initially converted 80% of the FCC available isobutene to MTBE. Pricing for methanol, field butane and related raw materials are given in Table 50.

As the isobutene content of the FCC total effluent is quite small, i.e. approx. 1.5%, associated MTBE production exclusively from this source will neither constitute a large volume nor make a significant octane impact upon the total refinery gasoline pool.

Further evidence of the negative FCC-based MTBE production economics as related to this study is given in Tables 45 and 46. This data shows that after the installation of the 1000 m^3/SD isomerization unit, the linear program predicted no ether octane enhancing processing was necessary, and, in fact, cut back upon MTBE production utilizing more of the FCC derived isobutene as alkylation feedstock.

Although this linear program and associated study conditions have denied the MTBE processing exclusively from FCC C_4 generated olefin feedstocks, it is well documented that MTBE is being produced for the purpose of octane enhancement. A review of the

CEH MTBE product publication (3) shows a great concentration of MTBE production on the U.S. Gulf coast where the combined ether processing of the isobutene-rich petrochemical steam cracker effluents coupled with FCC olefins can not only produce a larger volume of MTBE, but still leave an effective alkylation olefin-paraffin feed ratio balance due to the unreacted olefins remaining in the steam cracker effluents. Chemical byproduct economic incentives also occur during MTBE production. Isobutene is difficult to separate from butene-1. As butene-1 commands a relatively high olefin price as a petrochemical, separation of isobutene from butene-1 can be accomplished by first reacting isobutene with methanol to form MTBE.

The possibility of an economically productive role for MTBE in transportation fuels may fall into the application of specialty product formulation or as an "octane trimming blending component". For example, after lead phase down, refineries will naturally have more difficulty in maintaining octane quality. If this octane quality shortage is small, the purchase or production of MTBE could have economic advantage over the installation of other more expensive processes such as isomerization.

3.4.2 **TAME Economic Assessment**

Linear programming economic predictions for TAME processing (Table 44) shows a C_5 FCC ether production as profitable under the present refinery design with TEL and MMT being allowed. These savings are due essentially to the reduced TEL and MMT requirement (Table 45). However, after the installation of the isomerization unit in Base Case 2, the refinery had surplus octane processing capability and neither ether octane upgrading nor the anti-knock additives were required.

Unlike MTBE processing, Table 45 does show a very small positive octane-m^3/year contribution ranging from 0.7 to 1.0 for the TAME reactor effluent study cases when total FCC gasoline octane-m^3 data is compared to base cases. However, as the isoamylene content of the FCC total effluent is only about 1.5% with active olefin conversion estimated to be 43.5%, octane upgrading from such a process will not have a large effect upon the octane quality of the total gasoline blending pool, i.e. approx. 0.35 calculated ON.

The TAME process can therefore be considered as an octane trimming operation similar to the MTBE process. However, as previously mentioned, the economic benefits of an octane trimming operation are not readily apparent in this study.

3.4.3 Isomerization Process Economic Assessment

After the installation of the 1000 m^3/SD isomerization unit (Base Case 2), the DiH Overheads stream was octane upgraded by 5.1 to 6.9 X 10^6 octane-m^3/year in the four study cases examined (Table 45). This octane upgrade was sufficient to allow the refinery to dispense with other forms of octane improvement such as ether processes and synthetic additives.

Although the ROI for the $18,000,000 isomerization investment is approximately 11 years, the linear program indicated the installation of the unit was necessary based upon the fact that the low octane quality DiH naphtha could not be used for gasoline blending after the removal of TEL and MMT additive. Additional LP studies involving refinery flexibility, volume and mix of product sales and associated penalties would probably greatly enhance the economics of the isomerization installation.

However, before such a large capital investment could be pursued, the following less expensive avenues of octane upgrading would have to be exhausted:

i) The FCCU would be operated at a high severity with the appropriate high octane catalyst

ii) The reformer units would also be optimized at maximum octane severity.

iii) The crude and product slate would be altered in an effort to allow the reformer capacity to rise to the nominated design i.e. 3500 as opposed to 2300 m^3/SD (Table 48). This would involve negating the Jet B business and the purchase of higher naphtha content raw materials.

iv) The purchase or on-site manufacture of oxygenates such as MTBE could complement or provide the final octane trimming for the above three octane enhancement programs. Operation of the FCCU at high severity and with a high octane catalyst

could possibly provide the additional olefins necessary to allow the alkylation unit to remain at full capacity if an MTBE plant was interfaced into the refining environment.

3.4.4 Gasoline Blending

Gasoline blending volumetrics of premium and regular unleaded and regular leaded gasolines are given in Tables 52, 53 and 54, respectively.

The linear program in three out of four study cases deposits the entire MTBE production into regular unleaded gasoline. This blending procedure seemed unusual due to the high octane nature of MTBE; however, further investigation into the linear program blending logic showed MTBE to be more octane responsive to the presence of the large quantity of FCC gasoline contained in the regular unleaded than the large quantity of alkylate contained in the premium unleaded fuel.

3.4.5 Glossary of Economic Terms

After Tax ROI - The number of years required to recover project costs following payment of income tax at an estimated 50% of profits derived from this investment source.

Road Index - The sum of the actual Research and Motor Octane Values divided by two.

Octane - m^3 - The processed volume of the gasoline blending component times the calculated octane road index.

Octane - m^3/a - The annual processed volume of the gasoline blending component times the calculated octane road index.

m^3/CD - Cubic metres per calendar day (365 days/a).

m^3/SD - Cubic metres per stream day (approx. 300 days/a).

4. SUMMARY

4.1 MTBE

4.1.1 Based upon a FCC C_4 alkylation unit feed, process conditions for an 80% equilibrium conversion of isobutene to MTBE were determined using a one-pass, single fixed catalyst bed of Rexyn 101(H) cationic exchange resin as follows:

Reactor Temperature	= 100°C
$LHSV^{-h}$	= 1.5
Reactor Pressure	= 2.3 mPa
Methanol/Active Olefin Molar Ratio	= 1.1/1

4.1.2 Included in a $2,500,000 MTBE plant cost estimate for processing up to 700 m^3/day C_4 FCC feedstock is a reactor, a distillation tower to separate MTBE from C_4 hydrocarbons and methanol and a glycol extraction and associated stripping column for the ppm removal of unreacted methanol from the remaining C_4 hydrocarbons, destined for further processing in an alkylation unit.

4.1.3 MTBE gasoline product quality parameters were determined to be as follows:

Research Octane Blending Number	= 116
Motor Octane Blending Number	= 101
Reid Vapour Pressure (Additional n-Butane Requirement for 10% MTBE Blend)	= 1.0%
Distillation Restriction	= 15% max.

4.1.4 Linear programming economics denied the processing of MTBE exclusively from FCC olefins in all study cases, primarily due to isobutene competition with alkylation processing.

4.1.5 The role of MTBE purchase or on-site refinery FCC production may reside in the application of a final octane trimming operation or as a high octane additive to a specialty product.

4.2 TAME

4.2.1 Based upon a 25-50°C FCC C_5 feedstock, a 60.8% maximum equilibrium conversion of the available 15.3% L/v isoamylenes (2-Methyl Butene-1 and 2-Methyl Butene-2) to TAME was obtained using a one pass reaction with the same cationic exchange catalyst bed under the following conditions:

Reactor Temperature	= 65°C
$LHSV^{-h}$	= 0.5
Reactor Pressure	= 1.7 mPa
Methanol/Active Olefin Molar Ratio	= 1.1/1

4.2.2 With consideration to reactor size and the amount of unreacted methanol remaining in the TAME reactor product, the following process conditions yielding a 43.5% equilibrium conversion of isoamylenes to TAME were chosen:

Reactor Temperature	= 80°C
$LHSV^{-h}$	= 2.0
Reactor Pressure	= 1.7 mPa
Methanol/Active Olefin Molar Ratio	= 0.74/1

4.2.3 Based upon these process conditions (4.2.2), an estimated $500,000 cost for a TAME plant was established. As no unreacted methanol removal was necessary either from product quality or further processing considerations, this $500,000 plant consisted simply of a reactor and associated pumps and was designed to process approx. 500 m^3/d of a FCC C_5 feed. This cost does assume a methanol feed tank and appropriate transfer system are already on-site.

4.2.4 Percent isoamylene conversion to TAME appears related to the ratio of the two C_5 ether reactive olefins, 2-Methyl Butene-1 and 2-Methyl Butene-2 present in the feedstock with 2-Methyl Butene-1 being the preferred isoamylene for maximum TAME conversion.

4.2.5 TAME gasoline product quality parameters were determined to be as follows:

Research Octane Blending Number	= 106
Motor Octane Blending Number	= 99
Reid Vapor Pressure (Additional n-Butane Requirement for 10% TAME Blend)	= 1.0%
Distillation Restriction	= 25% max.

4.2.6 C_5 reactor effluent gasoline product quality parameters determined and calculated for the 43.5% process isoamylene conversion to TAME were as follows:

C_5 Reactor Feed 25-50°C (RON/MON)	= 95.3/84.0
C_5 Reactor Product (RON/MON)	= 96.3/85.8
Reid Vapor Pressure (Reduction in n-Butane Content for 10% Blend)	= 1.5%
Distillation Restriction	= 25% max.

4.2.7 Linear program economics indicated TAME processing to show a small profit under present design with TEL and MMT anti-knock additives being allowed into gasoline. The savings were essentially due to the reduced TEL and MMT requirement and showed an after tax return on investment in about 4 years.

4.2.8 Linear program economics following the anticipated legislated removal of anti-knock additives and the installation of an isomerization unit indicated the study case refinery had sufficient octane processing capabilities without any ether octane upgrading facilities.

4.2.9 The role of FCC-derived C_5 TAME reactor effluent could possibly be useful in an octane trimming situation.

4.3 THME

4.3.1 THME methoxylation was not selected as a process due to the low equilibrium conversion of isohexylenes and the low octane quality of the resulting THME.

4.3.2 Based upon a 50-75°C FCC C_6 feedstock, a 41.3% maximum equilibrium conversion of isohexylenes to THME was obtained using a single-pass fixed-bed reactor system under the following conditions:

Reactor Temperature	= 80°C
LHSV^{-h}	= 0.5
Reactor Pressure	= 1.7 mPa
Methanol/Active Olefin Molar Ratio	= 1.1/1

4.3.3 Pure THME (four compounds) was determined to have a RON value of 90.0 and a MON of 82.0. Published octane values

(31) indicated the eight C_6 ether precursors to have a RON range from 90.3 to 100.1 with a MON variation of 72.0 to 83.0.

4.3.4 The chemistry involved in the formation of THME is considerably more involved than MTBE or TAME; eight ether reactive C_6 olefins form four THME isomers. The equilibrium reactions are reversible in the temperature range of interest and considerable isomerization of some of the eight C_6 ether reactive olefins does occur.

4.4 Isomerization

4.4.1 Following the installation of the Isomerization process, the study case refinery possessed sufficient octane processing potential as to dispense with both ether processing and anti-knock additive octane enhancement.

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TABLE 1

GASOLINE-OXYGENATE BLENDS

	0.5:1 Methanol/IPA by volume blends				1:1 Methanol/IPA by volume blends				2:1 Methanol/IPA by volume blends			
	% Oxygen by wt	% Alcohol by vol	% Methanol by vol	% IPA by vol	% Oxygen by wt	% Alcohol by vol	% Methanol by vol	% IPA by vol	% Oxygen by wt	% Alcohol by vol	% Methanol by vol	% IPA by vol
RUL*	4.0	8.55	2.85	5.70	4.0	9.32	4.66	4.66	4.0	10.29	6.87	3.42
PUL*	4.0	8.64	2.88	5.76	4.0	9.42	4.71	4.71	4.0	10.41	6.95	3.46

Pure Methyl Tertiary Butyl Ether (MTBE) - Gasoline Blends

	1% O_2 by wt blends % MTBE by vol	2% O_2 by wt blends % MTBE by vol	4% O_2 by wt blends % MTBE by vol	6% O_2 by blends % MTBE by vol
RUL	5.3	10.2	18.8	26.2
PUL	5.4	10.3	19.0	26.4

Pure Tertiary Amyl Methyl Ether (TAME) - Gasoline Blends

	1% O_2 by wt blends % TAME by vol	2% O_2 by wt blends % TAME by vol	3% O_2 by wt blends % TAME by vol
RUL	5.88	11.20	16.04
PUL	5.95	11.30	16.2

TAME Reactor Product (14.8% by vol TAME) - Gasoline Blends

	1% O_2 by wt blends		2% O_2 by wt blends		3% O_2 by wt blends	
	% TAME by vol	% Reactor Product by vol	% TAME by vol	% Reactor Product by vol	% TAME by vol	% Reactor Product by vol
RUL	3.49	24.1	7.16	49.4	10.0	68.9
PUL	3.52	24.3	7.21	49.7	10.0	68.9

* RUL = Regular Unleaded Gasoline
PUL = Premium Unleaded Gasoline

TABLE 1

GASOLINE-OXYGENATE BLENDS Continued

Partially Purified TAME Reactor Product (50.0% by vol TAME) - Gasoline Blends

	1% O_2 by wt blends		2% O_2 by wt blends		3% O_2 by wt blends	
	% TAME by vol	% Reactor Product by vol	% TAME by vol	% Reactor Product by vol	% TAME by vol	% Reactor Product by vol
RUL	5.48	6.4	10.9	12.8	16.3	19.0
PUL	5.54	6.5	11.0	12.9	16.4	19.2

Pure Tertiary Hexyl Methane Ether (THME) - Gasoline Blends

	0.5% O_2 by wt blends	1% O_2 by wt blends
	% THME by vol	% THME by vol
RUL	2.75	5.84
PUL	2.79	5.91

THME Reactor Product (5.1% by vol THME) - Gasoline Blends

	1% O_2 by wt blends		2% O_2 by wt blends	
	% THME by vol	% Reactor Product by vol	% THME by vol	% Reactor Product by vol
RUL	2.36	46.5	4.58	90.0
PUL	2.38	46.8	4.58	90.2

* RUL = Regular Unleaded Gasoline
PUL = Premium Unleaded Gasoline

TABLE 2

COMPOSITIONAL ANALYSIS OF METHYL TERTIARY BUTYL ETHER FEEDSTOCK

(C_4 ALKYLATION PLANT CATALYTICALLY CRACKED HYDROCARBONS)

Component	%, liquid volume
Propane	0.10
Propene	0.53
Isobutane	38.6
n-Butane	10.7
Butene-1	12.3
Trans-2-Butene	12.8
Cis-2-Butene	8.56
1,3-Butadiene	0.31
Isopentane	4.44
n-Pentane	0.07
3-Methyl Butene-1	0.42
Trans-2-Pentene	0.11
Cis-2-Pentene	0.05
Pentene-1	0.28
Isobutene*	10.24
2-Methyl Butene-1**	0.38
2-Methyl Butene-2**	0.07
Total Liquid Volume %***	100.00

* MTBE Reactive Olefin

** TAME Reactive Olefin

*** Values computed by internal normalization to 100.0%.

TABLE 3

MTBE PRODUCTION RUN MASS BALANCE DATA

Test Conditions	Feed #1	Product #1	Feed #2	Product #2	Average Feed Values	Composite Sample (Total Product)
Reactor Temperature (°C)	-	100	-	100		100
LHSV-h	-	1.5	-	1.5		1.5
Reactor Pressure (mPa)	-	2.7	-	2.7		2.7
Methanol/Active Olefin Ratio (Molar)	-	1.16/1	-	1.20/1		1.18/1
Active C_4 (g/h) Isobutene	92.4	17.7*	91.6	15.1*	92.0	17.6*
Active C_5 (g/h)						
2 Methyl Butene-1	3.8	0.5	3.9	0.5	3.8	0.5
2 Methyl Butene-2	0.6	0.5	0.6	0.5	0.6	0.5
Methanol (g/h)	63.7	11.1	64.9	10.1	64.5	10.5
Products (g/h)						
Dimethyl Ether	N.D	2.9	N.D	2.4	N.D	1.9
MTBE	N.D	117.1	N.D	112.3	N.D	112.4
TAME	N.D	2.1	N.D	1.6	N.D	1.6
Mass Balance						
Based upon Total Feed	-	92.0	-	87.8	-	90.2
Based on Isobutene	-	99.9	-	94.5	-	97.0
Based on Methanol Consumption	-	91.5	-	86.0	-	84.5
Conversion						
Based on Isobutene	-	80.8	-	83.5	-	82.0
Based on MTBE produced	-	80.7	-	78.1	-	78.0

*Includes Isobutene in both product and LPG off gas
N.D. = Not Detected

TABLE 4

COMPOSITIONAL ANALYSIS OF MTBE FEED AND PRODUCT

Component	Feed (l/v%)	Final Product (l/v%)	Off-Gas By Product (Mass%)
Oxygen	-	-	0.53
Ethane	-	-	0.15
Ethene	-	-	0.20
Propane	0.10	0.024	1.47
Propene	0.53	0.23	0.67
Isobutane	38.6	29.6	46.3
Butene-1	12.3	9.48	9.52
1,3 Butadiene	0.31	0.21	0.71
n-Butane	10.7	10.3	12.8
Trans-2-Butene	12.8	12.7	12.8
Cis-2-Butene	8.56	8.61	8.64
2,2 Dimethyl Propane	-	0.02	-
3 Methyl Butene-1	0.42	0.50	-
Isopentane	4.44	5.64	3.26
Pentene-1	0.28	0.35	-
2 Methyl Butene-1	0.38	0.08	-
n-Pentane	0.07	0.10	-
Trans-2-Pentene	0.11	0.16	-
Cis-2-Pentene	0.05	0.07	-
2 Methyl Butene-2	0.07	0.07	-
Isobutene	10.24	2.48	2.49
MTBE	N.D	15.0	-
TAME	N.D	0.20	-
Methanol -	-	1.30	-
Dimethyl Ether	N.D	0.25	-
Other higher boiling hydrocarbons and unidentified oxygenates			
Pentenes	-	-	0.46
C6+	-	-	0.04

TABLE 5

SEPARATION OF METHANOL, METHYL TERTIARY BUTYL ETHER AND UNREACTED HYDROCARBON

Distillation	% Distilled (Liq Vol)	Methanol (% Liq Vol)	MTBE ~~TBME~~ (% Liq Vol)	Hydrocarbon (% Liq Vol)
IBP - 52°C	46.1	0.8	0.7.	98.5
52 - 56°C	21.8	3.4	59.9.	36.7
50 - 64°C	10.3	10.1	7.1	82.8
64 - 66°C	1.4	N.D.	N.D.	98.6
66 - 83°C	4.5	N.D.	N.D.	95.5
83°C	13.9	N.D.	N.D.	86.1
Loss	2.0	-	-	-
Feed	-	2.5	15.0	87.5

Boiling Points: Methanol = 65°C
MTBE = 55.2°C

Glycol Extraction

	0.5M Glycol* % by wt			0.25M Glycol* % by wt			0.125M Glycol* % by wt		
	Methanol	MTBE	HC**	Methanol	~~TBME~~ MTBE	~~MTBE~~ HC	Methanol	MTBE	HC**
Feed	3.53	53.4	43.1	3.53	53.4	43.1	3.53	53.4	43.1
Product	0.98	58.6	41.4	1.70	57.8	40.5	2.47	57.4	40.1

* 0.5M, 025M and 0.125M molar ratios of Glycol/Reactor product were separately extracted

** HC = Hydrocarbon

TABLE 5 Continued

SEPARATION OF METHANOL, METHYL TERTIARY BUTYL ETHER AND UNREACTED HYDROCARBON

Molecular Sieve Adsorption

Sieve Type		= 4a
Mesh Size		= 40 - 60 mesh
Adsorber Dimensions		
	Height	= 25 cm
	Diameter	= 0.8 cm
	Volume	= 12.56 mL
Wt of Sieve		= 11.0 g
Flow Rate		= 0.32 mL/min
Contact Time		= 39.3 min
Temperature		= 23°C

Volume Processed (mL)	Methanol (% Liq Vol)	MTBE ~~THME~~ (% Liq Vol)	Hydrocarbon (% Liq Vol)
30	2.3.	52.2	45.5
60	2.8	53.6	43.6
160	3.0	54.5	42.5
270	3.2	54.1	42.7
Feed	3.1	50.6	46.3

TABLE 6

BLENDING DATA FOR

PREMIUM UNLEADED MOGAS/MeOH/IPA BLENDS

Blend Composition % vol:				
Premium Unleaded	100.0	90.58	91.36	89.59
MeOH/IPA	0	9.42	8.64	10.41
MeOH:IPA Ratio	0	1.00	2.00	0.50
Oxygen Content, % wt	0	4.0	4.0	4.0
Blend Research ON	96.2	98.8	98.7	98.9
Blend Motor ON	86.4	87.6	87.5	87.6
Delta Res ON over basefuel	0	2.6	2.5	2.7
Delta Motor ON over basefuel	0	1.2	1.1	1.2
Blending Res ON	-	123.8	125.1	122.1
Blending Motor ON	-	99.2	99.1	97.9
Blending Sensitivity	-	24.6	26.0	24.2
Reid Vapour Pressure, kPa	54.6	59.4	71.9	60.8
D867 Distillation, °C				
IBP	46	37	37	38
10% evap. @	78	52	50	53
50% evap. @	116	108	109	106
90% evap. @	166	161	163	162
FBP	206	202	205	204
Recovery, % vol	98	98.2	96.5	96.5
Residue, % vol	0.8	0.4	0.7	0.7
Loss, % vol	1.2	1.4	2.3	2.8
Phase Separation Temperature °C	<-40.0	<-40.0	<-40.0	<-40.0

-

TABLE 7

BLENDING DATA FOR

REGULAR UNLEADED MOGAS/MeOH/IPA BLENDS

Blend Composition % vol:				
Regular Unleaded	100.0	90.68	91.45	89.71
MeOH/IPA	0	9.32	8.55	10.29
MeOH:IPA Ratio	0	1.00	2.00	0.50
Oxygen Content, % wt	0	4.0	4.0	4.0
Blend Research ON	94.2	96.9	96.5	96.9
Blend Motor ON	83.8	84.5	84.7	84.9
Delta Res ON over basefuel	0	2.7	2.3	2.7
Delta Motor ON over basefuel	0	0.7	0.9	1.1
Blending Res ON	-	123.2	121.1	120.4
Blending Motor ON	-	91.3	94.3	94.5
Blending Sensitivity	-	31.8	26.8	25.9
Reid Vapour Pressure, kPa	81.9	91.6	96.0	91.2
D867 Distillation, °C				
IBP	32	29	27	28
10% evap. @	53	40	42	40
50% evap. @	112	93	93	97
90% evap. @	181	176	176	176
FBP	216	214	215	213
Recovery, % vol	98.5	95.1	97.5	96.0
Residue, % vol	0.6	0.4	0.5	1.0
Loss, % vol	0.9	4.5	2.0	3.0
Phase Separation Temperature °C	<-40.0	<-40.0	<-40.0	<-40.0

TABLE 8

BLENDING DATA FOR

PREMIUM UNLEADED MOGAS/MTBE BLENDS

Blend Composition % vol:					
Premium Unleaded	100.0	94.6	89.7	81.0	73.6
MTBE	0	5.4	10.30	19.00	26.4
Oxygen Content, % wt	0	1.0	2.0	4.0	6.0
Blend Research ON	96.2	97.2	98.3	99.8	100.8
Blend Motor ON	86.4	87.6	87.9	88.9	90.2
Delta Res ON over basefuel	0	1.0	2.1	3.6	4.6
Delta Motor ON over basefuel	0	1.2	1.5	2.5	3.8
Blending Res ON	0	114.7	116.6	115.2	113.6
Blending Motor ON	0	108.6	101.0	99.6	100.8
Blending Sensitivity	0	6.1	15.6	15.6	12.8
Reid Vapour Pressure, kPa	54.6	51.1	51.5	50.8	54.2
D867 Distillation, °C					
IBP	46	34	36	35	37
10% evap. @	78	64	59	58	57
50% evap. @	116	111	107	99	92
90% evap. @	166	164	162	160	158
FBP	206	201	200	204	197
Recovery, % vol	98.0	98.7	97.9	99.0	98.7
Residue, % vol	0.8	0.8	0.9	0.4	0.9
Loss, % vol	1.2	0.5	1.2	0.6	0.4
Phase Separation Temperature °C	<-40.0	-18.5	-21.0	-26.5	-36.5

TABLE 9

BLENDING DATA FOR

REGULAR UNLEADED MOGAS/MTBE BLENDS

Blend Composition % vol:					
Regular Unleaded	100.0	94.7	89.8	81.2	74.8
MTBE	0	5.3	10.2	18.8	26.2
Oxygen Content, % wt	0	1.0	2.0	4.0	6.0
Blend Research ON	94.2	95.0	96.4	98.0	99.4
Blend Motor ON	83.8	84.7	85.1	86.4	87.9
Delta Res ON over basefuel	0	0.8	2.2	3.8	5.2
Delta Motor ON over basefuel	0	0.9	1.3	2.6	4.1
Blending Res ON	0	109.3	115.8	114.4	114.1
Blending Motor ON	0	100.8	96.6	97.6	99.5
Blending Sensitivity	0	8.5	19.2	16.8	14.6
Reid Vapour Pressure, kPa	81.9	77.7	78.3	76.7	68.3
D867 Distillation, °C					
IBP	32	29	29	28	32
10% evap. @	53	45	45	45	47
50% evap. @	112	102	97	87	79
90% evap. @	181	178	176	175	169
FBP	216	213	212	213	208
Recovery, % vol	98.5	96.5	97.4	98.6	98.0
Residue, % vol	0.6	1.0	1.1	0.4	1.0
Loss, % vol	0.9	2.5	1.5	1.0	1.0
Phase Separation Temperature °C	<-40.0	-21.0	-21.8	-28.8	-35.8

TABLE 10

BUTANE DISPLACEMENT EFFECTS ON UNLEADED MOGAS/MTBE BLENDS

RVP data in Tables 8 and 9 is summarized below as a function of RVP vs. l/v % nC_4 back in (or back out) using Figure 3.

% vol MTBE		RVP kPa (psig)		RVP as l/v % nC_4	l/v of nC_4 Back In (Back Out)
Regular Unleaded	- 0	81.9	(11.9)	14.9	0
Regular Unleaded	+ 5.3%	77.7	(11.3)	13.6	+1.3
Regular Unleaded	+ 10.2%	78.3	(11.4)	13.8	+1.1
Regular Unleaded	+ 18.8%	76.7	(11.1)	13.1	+1.8
Regular Unleaded	+ 26.2%	68.8	(10.0)	10.8	+4.1
Premium Unleaded	- 0	54.6	(7.9)	6.3	0
Premium With Lead	+ 5.4%	51.1	(7.4)	5.1	+1.2
Premium With Lead	+ 10.3%	51.5	(7.5)	5.5	+0.8
Premium With Lead	+ 19.0%	50.8	(7.4)	5.1	+1.2
Premium With Lead	+ 26.4%	51.2	(7.4)	5.1	+1.2

Therefore, for a blend of unleaded mogas with 5-10% l/v MTBE, approximately 1.0% l/v additional n-butane is required to maintain the original RVP.

TABLE 11

HYDROCARBON COMPOSITION AND WATER CONTENT OF GASOLINE BLENDING STOCKS

	Regular Unleaded Gasoline % liquid volume	Premium Unleaded Gasoline % liquid volume
Paraffins	54.2	61.2
Monocycloparaffins	9.2	3.3
Dicycloparaffins	0.6	0.0
Tricycloparaffins	0.3	0.0
Monoolefins	11.9	5.1
Cycloolefins	2.1	1.1
Dicycloolefins	0.2	0.1
Alkylbenzenes	20.9	28.5
Indans	0.5	0.4
Indenes	0.1	0.2
Naphthalenes	0.0	0.1
Water, ppm (Karl Fischer)	52	81

MTBE, ppm w/w H_2O = 155

C_5 Reactor Effluent, ppm w/w H_2O = 920

C_6 Reactor Effluent, ppm w/w H_2O = 297

TABLE 12

COMPOSITIONAL ANALYSIS OF METHYL TERTIARY AMYL ETHER FEEDSTOCK

(C_5 CATALYTICALLY CRACKED GASOLINE FRACTION 25-50°C)

Component	%, liquid volume
Isobutane	0.03
n-Butane	0.15
Butene-1	0.08
Trans-2-Butene	0.17
Cis-2-Butene	0.22
Isopentane	43.5
n-Pentane	7.45
3-Methyl Butene-1	0.34
Trans-2-Pentene	6.91
Cis-2-Pentene	3.73
Pentene-1	2.25
1,2-Pentadiene	0.05
Cis-1,3-Pentadiene	0.06
2,3-Pentadiene	0.50
2-Methyl Butadiene	0.04
Pentene-1	0.07
Cyclopentane	0.79
Cyclopentene	1.25
2,2-Dimethyl Butane	0.13
2,3-Dimethyl Butane	1.86
2-Methyl Pentane	6.72
3-Methyl Pentane	2.82
n-Hexane	N.D.
C_6 Olefin	0.36
Trans-2-Hexene + 3-Methyl Cyclopentene	0.35
Cis-2-Hexene	0.12
Cis/Trans-3-Hexene	0.19
Hexene-1	0.45
2,4-Dimethyl Pentane	0.05
Methyl Cyclopentane + 2,2-Dimethyl Pentane	0.78
Benzene	0.31
2-Methyl Butene-1*	4.72
2-Methyl Butene-2*	10.60
2,3-Dimethyl Butene-1**	0.15
2-Methyl Pentene-1**	0.41
2-Methyl Pentene-2**	0.32
Cis-3-Methyl Pentene-2**	0.25
Trans-3-Methyl Pentene-2**	0.20
Total Liquid Volume %***	98.38

* TAME Reactive Olefin
** THME Reactive Olefin
*** Values computed from a Methyl Ethyl Ketone Internal Standard

TABLE 13

C_5 OPTIMIZATION EXPERIMENTS

Test Conditions	Feed	Run #1	Run #2	Run #3	
Reactor Temperature (°C)	-	65	80	95	
LHSV-h	-	0.5	0.5	0.5	
Reactor Pressure (mPa)	-	1.7	1.7	1.7	
Methanol/Active Olefin Ratio (Molar)	-	1.09/1	1.09/1	1.09/1	
Active C_4 (g/h)	0.02	N.D.	N.D.	N.D.	
Isobutene	0.02	N.D.	N.D.	N.D.	
Active C_5 (g/h)	4.68	1.93	2.09	2.88	
2-Methyl Butene-1	1.43	0.19	0.21	0.31	
2-Methyl Butene-2	3.25	1.74	1.88	2.55	
Active C_6 (g/h)	0.27	0.12	0.13	0.16	
2-Methyl Pentene-1	0.10	0.03	0.01	0.01	
2-Methyl Pentene-2	0.05	0.03	0.06	0.08	
Cis-3-Methyl Pentene-2	0.04	0.03	0.03	0.03	
Trans-3-Methyl Pentene-2	0.06	0.03	0.03	0.04	
2,3-Dimethyl Butene-1	N.D.	N.D.	N.D.	N.D.	
2,3-Dimethyl Butene-2	N.A.	N.A.	N.A.	N.D.	
2-Ethyl Butene-1	0.02	N.D.	N.D.	N.D.	
1-Methyl Cyclopentene-1	N.D.	N.D.	N.D.	N.D.	
Methanol (g/h)	2.44	0.86	0.83	0.76	
Products (g/h)					
Dimethyl Ether	N.D.	0.02	0.09	0.33	
MTBE	N.D.	0.05	0.02	0.01	
TAME	N.D.	4.18	3.81	2.65	
THME	N.D.	0.15	0.13	0.09	
Elemental Analysis					
Nitrogen, ppm w/w as N	9.7	8	2	2	
Sulfur, ppm w/w as S	25	10	4	2	
Oxygen, % w/w as O_2 -	N.D.	3.5	3.3	2.8	
Gravity kg/L @ 15°C	0.6460	0.6594	0.6581	0.6559	
Mass Balance					
Based upon Total Feed	-	98.6	99.5	98.3	
Based on Total Active C_5	-	102.6	100.6	100.4	
Based on Total Methanol Consumption	-	92.6	90.6	85.3	
Conversion					
Based on 2-Methyl Butene-1	-	86.7	85.3	78.3	
Based on 2-Methyl Butene-2	-	46.5	42.2	21.5	
Based on Active C_5	-	58.8	55.3	38.5	

N.D. = Not Detected
N.A. = Not Available

TABLE 14

C_5 OPTIMIZATION EXPERIMENTS

Test Conditions	Feed	Run #4	Run #5	Run #6
Reactor Temperature (°C)	-	65	80	95
LHSV-h	-	2.0	2.0	2.0
Reactor Pressure (mPa)	-	1.7	1.7	1.7
Methanol/Active Olefin Ratio (Molar)	-	1.09/1	1.09/1	1.09/1
Active C_4 (g/h)	0.08	N.D.	N.D.	N.D.
Isobutene	0.08	N.D.	N.D.	N.D.
Active C_5 (g/h)	18.72	10.72	9.25	10.04
2-Methyl Butene-1	5.72	1.75	10.8	1.12
2-Methyl Butene-2	13.00	8.97	8.17	8.92
Active C_6 (g/h)	1.08	0.61	0.53	0.61
2-Methyl Pentene-1	0.40	0.20	0.12	0.08
2-Methyl Pentene-2	0.20	0.18	0.22	0.27
Cis-3-Methyl Pentene-2	0.16	0.13	0.07	0.12
Trans-3-Methyl Pentene-2	0.24	0.10	0.12	0.14
2,3-Dimethyl Butene-1	N.D.	N.D.	N.D.	N.D.
2,3-Dimethyl Butene-2	N.A.	N.A.	N.A.	N.A.
2-Ethyl Butene-2	0.08	N.D.	N.D.	N.D.
1-Methyl Cyclopentene-1	N.D.	N.A.	N.A.	N.A.
Methanol (g/h)	9.76	6.05	4.82	4.61
Products (g/h)				
Dimethyl Ether	N.D.	0.07	0.15	0.36
MTBE	N.D.	0.33	0.19	0.12
TAME	N.D.	12.00	14.75	12.49
THME	N.D.	0.34	0.42	0.38
Elemental Analysis				
Nitrogen, ppm w/w as N	9.7	8	4	4
Sulfur, ppm w/w as S	25	2	2	6
Oxygen, % w/w as O2	N.D.	3.9	3.7	3.4
Gravity kg/L @ 15°C	0.6460	0.6564	0.6569	0.6565
Mass Balance				
Based upon Total Feed	-	99.0	98.9	98.6
Based on Total Active C_5	-	101.3	103.6	99.5
Based on Total Methanol Consumption	-	103.7	106.5	94.0
Conversion				
Based on 2-Methyl Butene-1	-	69.4	81.3	80.4
Based on 2-Methyl Butene-2	-	31.0	37.2	31.4
Based on Active C_5	-	42.7	50.6	46.4

N.D. = Not Detected
N.A. = Not Available

TABLE 15

C_5 OPTIMIZATION EXPERIMENTS

Test Conditions	Feed	Run #7	Run #8	Run #9	
Reactor Temperature (°C)	-	65	80	95	
LHSV-h	-	0.5	0.5	0.5	
Reactor Pressure (mPa)	-	1.7	1.7	1.7	
Methanol/Active Olefin Ratio (Molar)	-	0.74/1	0.74/1	0.74/1	
Active C_4 (g/h)	0.02	N.D.	N.D.	N.D.	
Isobutene	0.02	N.D.	N.D.	N.D.	
Active C_5 (g/h)	4.71	2.11	2.43	3.29	
2-Methyl Butene-1	1.44	0.12	0.24	0.36	
2-Methyl Butene-2	3.27	1.99	2.19	2.93	
Active C_6 (g/h)	0.21	0.15	0.16	0.19	
2-Methyl Pentene-1	0.10	0.03	0.02	0.03	
2-Methyl Pentene-2	0.05	0.06	0.07	0.09	
Cis-3-Methyl Pentene-2	0.04	0.03	0.03	0.03	
Trans-3-Methyl Pentene-2	0.02	0.03	0.04	0.04	
2,3-Dimethyl Butene-1	N.D.	N.D.	N.D.	N.D.	
2,3-Dimethyl Butene-2	N.A.	N.A.	N.A.	N.A.	
2-Ethyl Butene-1	N.D.	N.D.	N.D.	N.D.	
1-Methyl Cyclopentene-1	N.A.	N.A.	N.A.	N.A.	
Methanol (g/h)	1.67	0.34	0.55	0.44	
Products (g/h)					
Dimethyl Ether	N.D.	0.02	0.06	0.27	
MTBE	N.D.	0.05	0.02	0.05	
TAME	N.D.	4.09	3.71	2.22	
THME	N.D.	0.12	0.12	0.07	
Elemental Analysis					
Nitrogen, ppm w/w as N	9.7	3	3	1	
Sulfur, ppm w/w as S	25	1	2	2	
Oxygen, % w/w as O_2	N.D.	2.6	2.7	2.1	
Gravity kg/L @ 15°C	0.6460	0.6565	0.6555	0.6539	
Mass Balance					
Based upon Total Feed	-	98.1	95.1	97.4	
Based on Total Active C_5	-	104.5	105.7	102.3	
Based on Total Methanol Consumption	-	101.9	110.0	107.6	
Conversion					
Based on 2-Methyl Butene-1	-	91.7	83.3	75.0	
Based on 2-Methyl Butene-2	-	39.1	33.3	10.4	
Based on Active C_5	-	53.1	48.4	30.1	

N.D. = Not Detected
N.A. = Not Available

TABLE 16

C_5 OPTIMIZATION EXPERIMENTS

Test Conditions	Feed	Run #10	Run #11	Run #12
Reactor Temperature (°C)	-	65	80	95
LHSV-h	-	0.5	0.5	0.5
Reactor Pressure (mPa)	-	1.7	1.7	1.7
Methanol/Active Olefin Ratio (Molar)	-	0.74/1	0.74/1	0.74/1
Active C_4 (g/h)	0.08	N.D.	N.D.	N.D.
Isobutene	0.08	N.D.	N.D.	N.D.
Active C_5 (g/h)	18.82	12.27	10.64	12.26
2-Methyl Butene-1	5.74	2.25	1.36	1.43
2-Methyl Butene-2	13.08	10.02	9.28	10.83
Active C_6 (g/h)	0.82	0.69	0.70	0.62
2-Methyl Pentene-1	0.39	0.24	0.15	0.10
2-Methyl Pentene-2	0.19	0.21	0.28	0.24
Cis-3-Methyl Pentene-2	0.15	0.14	0.13	0.13
Trans-3-Methyl Pentene-2	0.09	0.10	0.14	0.15
2,3-Dimethyl Butene-1	N.D.	N.D.	N.D.	N.D.
2,3-Dimethyl Butene-2	N.A.	N.A.	N.A.	N.A.
2-Ethyl Butene-1	N.D.	N.D.	N.D.	N.D.
1-Methyl Cyclopentene-1	N.A.	N.A.	N.A.	N.A.
Methanol (g/h)	6.68	2.83	2.21	2.32
Products (g/h)				
Dimethyl Ether	N.D.	N.D.	0.12	0.40
MTBE	N.D.	0.39	0.25	0.15
TAME	N.D.	10.82	12.83	10.15
THME	N.D.	0.31	0.35	0.31
Elemental Analysis				
Nitrogen, ppm w/w as N	9.7	6	5	3
Sulfur, ppm w/w as S	25	4	4	2
Oxygen, % w/w as O_2	N.D.	2.5	1.8	2.3
Gravity kg/L @ 15°C	0.6460	0.6517	0.6542	0.6528
Mass Balance				
Based upon Total Feed	-	100.0	99.8	98.4
Based on Total Active C_5	-	104.7	103.4	102.2
Based on Total Methanol Consumption	-	96.6	98.7	93.0
Conversion				
Based on 2-Methyl Butene-1	-	60.8	76.3	75.1
Based on 2-Methyl Butene-2	-	23.4	29.1	17.2
Based on Active C_5	-	34.8	43.5	34.9

N.D. = Not Detected
N.A. = Not Available

TABLE 17

VARIATION IN METHANOL/ACTIVE C_5 OLEFIN MOLAR RATIO

@ FEED = 480 m^3/d C_5 FCC GASOLINE

REACTOR TEMPERATURE = 80°C

$LHSV^{-h}$ = 2.0

REACTOR PRESSURE = 1.7 mPa

Methanol/Active Olefin Molar Ratio	% Conversion	TAME Production m^3/d	Methanol Feed Requirement m^3/d	Methanol Content % l/v in Reactor Effluent	% Loss in Fuel Volume
1.1/1	50.6	45.9	30.4	2.8	1.0
0.74/1	43.5	39.4	20.5	1.2	0.9

TABLE 18

TAME PRODUCTION RUN MASS BALANCE DATA

Test Conditions	Feed #1	Product #1	Feed #2	Product #2	Feed #3	Product #3	Average Feed Values	Composite Sample (Total Product)
Reactor Temperature (°C)	-	65	-	65	-	65	-	65
LHSV-h	-	0.5	-	0.5	-	0.5		0.5
Reactor Pressure (mPa)	-	1.7	-	1.7	-	1.7	-	1.7
Methanol/Active Olefin Ratio (Molar)	-	1.08	-	1.09	-	1.08	-	1.04
Active C_4 (g/h) Isobutene	-	-	-	-	-	-	-	-
Active C_5 (g/h)	(46.52)	(17.92)	(48.52)	(19.11)	(47.08)	(18.46)	(47.41)	(18.59)
2 Methyl Butene-1	14.19	1.72	14.78	1.79	14.07	1.73	14.44	1.76
2 Methyl Butene-2	32.33	16.20	33.74	17.32	33.01	16.73	32.97	16.83
Active C_6 (g/h)	(4.13)	(2.37)	(4.45)	(2.88)	(4.27)	(2.83)	(4.24)	(2.80)
2-Methyl Pentene-1	1.29	0.01	1.36	0.30	1.32	0.31	1.31	0.30
2-Methyl Pentene-2	1.00	0.85	1.07	0.91	1.03	0.90	1.02	0.90
Cis-3-Methyl Pentene-2	0.77	0.59	0.83	0.65	0.80	0.63	0.79	0.63
Trans-3-Methyl Pentene-2	0.64	0.66	0.70	0.74	0.66	0.71	0.65	0.70
2,3-Dimethyl Butene-1	0.43	0.26	0.49	0.28	0.46	0.28	0.47	0.27
2,3-Dimethyl Butene-2	N.A.	-	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
2-Ethyl Butene-2	N.A.	-	-	-	N.A.	N.A.	N.A.	N.A.
1-Methyl Cyclopentene-1	N.A.	-	-	-	N.A.	N.A.	N.A.	N.A.
Methanol (g/h)	24.52	7.67	25.95	10.08	24.93	8.03	24.27	9.08
Products (g/h)								
Dimethyl Ether	N.D.	0.29	N.D.	0.33	N.D.	0.26	N.D.	0.30
MTBE	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
TAME	N.D.	45.86	N.D.	49.30	N.D.	48.28	N.D.	48.15
THME	N.D.	2.93	N.D.	3.51	N.D.	3.13	N.D.	3.33
Elemental Analysis								
Nitrogen, ppm w/w as N	9.7	-	9.7	-	9.7	-	9.7	-
Sulfur, ppm w/w as S	25	-	25	-	25	-	25	-
Oxygen, % w/w as O_2	N.D.	3.5	N.D.	4.1	N.D.	3.7	N.D.	3.9
Gravity kg/L @ 15°C	0.6460	-	0.6460	-	0.6460	0.6394		
Mass Balance								
Based upon Total Feed	-	99.5	-	98.9	-	99.2	-	99.2
Based on Active C_5	-	106.2	-	109.2	-	109.7	-	109.0
Based on Methanol Consumption	-	94.7	-	104.0	-	97.9	-	105.2
Conversion								
Based on 2-Methyl Butene-1	-	87.9	-	87.9	-	88.0	-	87.8
Based on 2-Methyl Butene-2	-	50.2	-	48.7	-	49.3	-	49.0
Based on Active C_5	-	61.9	-	60.6	-	60.8	-	60.8

N.D. = Not Detected
N.A. = Not Available

TABLE 19

COMPOSITIONAL ANALYSIS OF TAME FEED AND PRODUCT

Component	Feed (L/V %)	Final Product (L/V %)
Isobutane	0.03	0.03
Butene-1	0.08	0.04
Isobutene	N/D	N/D
n-Butane	0.14	0.15
Trans-2-Butene	0.16	0.18
Cis-2-Butene	0.21	0.22
3-Methyl Butene-1	0.34	0.38
Isopentane	40.2	40.1
Pentene-1	2.10	2.10
n-Pentane	6.45	7.15
2-Methyl Butadiene	0.04	N/D
Trans-2-Pentene	6.55	6.98
Pentyne-1	0.07	0.08
Cis-2-Pentene	3.48	3.77
Cis-1,3-Pentadiene	0.06	0.02
1,2-Pentadiene	0.05	0.13
2,2-Dimethyl Butane	0.12	N/D
Cyclopentene	1.19	1.10
2,3-Pentadiene	0.44	0.47
Cyclopentane	0.74	0.72
2,3-Dimethyl Butane	1.74	1.93
2,3-Dimethyl Butene-1	0.14	0.08
2-Methyl Pentane	6.27	6.49
C_6 Olefin	0.34	0.35
3-Methyl Pentane	2.54	2.80
2-Methyl Pentene-1	0.38	0.09
Hexene-1	0.14	0.16
n-Hexane	0.42	0.38
2-Ethyl Butene-1	N/D	N/D
Cis/Trans Hexene-3	0.18	0.20
3-Methyl Cyclopentene + Trans-2-Hexene	0.33	0.37
2-Methyl Pentene-2	0.30	0.26
Cis-3-Methyl Pentene-2	0.23	0.18
Cis-2-Hexene	0.11	0.12
Trans-3-Methyl Pentene-2	0.19	0.20
Methyl Cyclopentane + 2,2-Dimethyl Pentane	0.73	0.71
2,4-Dimethyl Pentane	0.05	0.15
Benzene + 1-Methyl Cyclopentene-1	0.29	0.28
MTBE	N/D	N/D
TAME	N/D	12.54
Total THME	N/D	0.80
2-Methyl Butene-1	4.41	0.53
2-Methyl Butene-2	9.88	5.01
Methanol	6.13	2.03
Dimethyl Ether	N/D	0.07

TABLE 20

SEPARATION OF METHANOL, TAME AND UNREACTED HYDROCARBON

Distillation	% Distilled (Liq Vol)	Methanol (% Liq Vol)	THME (% Liq Vol)	Hydrocarbon (% Liq Vol)
IBP - 64°C	83.8	1.24	0.01	98.7
64 - 66°C	4.8	N.D.	1.37	98.6
66 - 86°C	2.7	N.D.	48.4	51.6
86°C+	8.1	N.D.	83.2	16.8
Loss	0.6	-	-	-
Feed	-	1.55	8.66	89.8

Boiling Points - Methanol = 65°C
TAME = 86.3°C

Glycol Extraction

	0.5M Glycol* % by wt			0.25M Glycol* % by wt			0.125M Glycol* % by wt		
	Methanol	TAME	HC**	Methanol	TAME	HC**	Methanol	TAME	HC**
Feed	1.87	10.2	87.9	1.87	10.2	87.9	1.87	10.2	87.9
Product	N.D.	10.2	89.8	0.13	10.2	89.7	0.21	10.3	89.5

* 0.5M, 025M and 0.125M molar ratios of Glycol/Reactor product were separately extracted

** HC = Hydrocarbon

TABLE 20 Continued

SEPARATION OF METHANOL, TAME AND UNREACTED HYDROCARBON

Molecular Sieve Adsorption

Sieve Type		= 4a
Mesh Size		= 40 - 60 mesh
Adsorber Dimensions		
	Height	= 25 cm
	Diameter	= 0.8 cm
	Volume	= 12.56 mL
Wt of Sieve		= 11.0 g
Flow Rate		= 0.32 mL/min
Contact Time		= 39.3 min
Temperature		= 23°C

Volume Processed (mL)	Methanol (% Liq Vol)	THME (% Liq Vol)	Hydrocarbon (% Liq Vol)
30	0.42	12.7	86.9
80	0.80	12.5	86.7
160	1.75	12.9	85.3
250	1.87	12.8	85.3
330	2.01	12.5	85.5
500	1.93	12.8	85.3
580	1.98	12.7	85.3
Feed	2.05	12.6	85.3

TABLE 21

METHANOL REMOVAL BY RECYCLE OF C5 REACTOR PRODUCT

Parameter	Feed	Run #1	
Test Conditions			
Reactor Temperature (°C)	-	65	
LHSV-h	-	0.5	
Reactor Pressure (psig)	-	250	
Methanol/Active Olefin Ratio (Molar)	-	0.69/1	
Active C_4 (g/h)	N.D.	N.D.	
Isobutene		N.D.	N.D.
Active C_5 (g/h)	2.84	2.06	
2-Methyl Butene-1		0.34	0.18
2-Methyl Butene-2		2.50	1.88
Active C_6 (g/h)	0.17	0.14	
2-Methyl Pentene-1		0.03	0.01
2-Methyl Pentene-2		0.07	0.07
Cis-3-Methyl Pentene-2		0.03	0.03
Trans-3-Methyl Pentene-2		0.04	0.03
2,3-Dimethyl Butene-1		N.D.	N.D.
2,3-Dimethyl Butene-2		N.A.	N.A.
2-Ethyl Butene-2		N.D.	N.D.
1-Mehyl Cyclopentene-1		N.D.	N.D.
Methanol (g/h)		0.94	0.58
Products (g/h)			
Dimethyl Ether		0.09	0.10
MTBE		0.04	0.02
TAME		3.11	4.37
THME		0.10	0.13
Elemental Analysis			
Nitrogen, ppm w/w as N		3	2
Sulfur, ppm w/w as S		3	3
Oxygen, % w/w as O_2		3.1	3.2
Gravity kg/L @ 15°C		0.6560	0.6579
Mass Balance			
Based upon Total Feed		-	97.4
Based on Active C_5		-	103
Based on Methanol Consumption		-	105.3
Conversion			
Based on 2-Methyl Butene-1		-	47.1
Total on 2-Methyl Butene-2		-	24.8
Based on Active C_5		-	27.5

N.D. = Not Detected
N.A. = Not Available

TABLE 22

BLENDING DATA FOR

PREMIUM UNLEADED MOGAS/TAME BLENDS

Blend Composition % vol:				
Premium Unleaded	100.0	94.05	88.7	83.8
TAME	0	5.95	11.3	16.2
Oxygen Content, % wt	0	1.0	2.0	3.0
Blend Research ON	96.2	96.0	96.8	98.2
Blend Motor ON	86.4	87.0	87.8	88.3
Delta Res ON over basefuel	0	-0.2	0.6	2.0
Delta Motor ON over basefuel	0	0.6	1.4	1.9
Blending Res ON	0	92.8	101.5	108.6
Blending Motor ON	0	96.5	98.8	98.1
Blending Sensitivity	0	-3.7	2.7	10.4
Reid Vapour Pressure, kPa	54.6	51.1	52.5	47.7
D867 Distillation, °C				
IBP	46	40	38	40
10% evap. @	78	68	71	71
50% evap. @	116	111	109	106
90% evap. @	166	164	161	162
FBP	206	205	204	202
Recovery, % vol	98.0	98.2	99.4	98.5
Residue, % vol	0.8	0.7	0.4	0.9
Loss, % vol	1.2	1.1	0.2	0.6
Phase Separation Temperature °C	<-40.0	-20.5	-21.8	-26.5

TABLE 23

BLENDING DATA FOR

REGULAR UNLEADED MOGAS/TAME BLENDS

Blend Composition % vol:				
Regular Unleaded	100.0	94.12	88.8	84.0
TAME	0	5.88	11.2	16.0
Oxygen Content, % wt	Nil	1.0	2.0	3.0
Blend Research ON	94.2	95.0	96.0	95.6
Blend Motor ON	83.8	84.5	85.1	85.6
Delta Res ON over basefuel	0	0.8	1.8	1.4
Delta Motor ON over basefuel	0	0.7	1.3	1.8
Blending Res ON	0	107.8	110.3	103.0
Blending Motor ON	0	95.7	95.4	95.0
Blending Sensitivity	0	12.1	14.9	8.0
Reid Vapour Pressure, kPa	81.9	78.8	75.7	70.1
D867 Distillation, °C				
IBP	32	28	30	32
10% evap. @	53	49	52	54
50% evap. @	112	105	103	101
90% evap. @	181	178	177	175
FBP	216	214	216	213
Recovery, % vol	98.5	98.0	98.2	99.0
Residue, % vol	0.6	0.4	0.3	0.4
Loss, % vol	0.9	1.6	1.5	0.6
Phase Separation Temperature °C	<-40.0	-19.0	-26.5	-25.0

TABLE 24

BLENDING DATA FOR

PREMIUM UNLEADED MOGAS/C_5 REACTOR EFFLUENT

Blend Composition % vol:				
Premium Unleaded	100.0	75.7	50.3	31.1
C_5 Reactor Effluent	0	24.3	49.7	68.9
Oxygen Content, % wt	Nil	1.0	2.0	3.0
Blend Research ON	96.2	96.6	96.8	96.9
Blend Motor ON	86.4	86.5	86.8	86.6
Delta Res ON over basefuel	0	0.4	0.6	0.7
Delta Motor ON over basefuel	0	0.1	0.4	0.2
Blending Res ON	0	97.9	97.4	97.2
Blending Motor ON	0	86.8	87.2	86.7
Blending Sensitivity	0	11.1	10.2	10.5
Reid Vapour Pressure, kPa	54.6	73.9	81.5	87.8
D867 Distillation, °C				
IBP	46	33	31	29
10% evap. @	78	43	42	38
50% evap. @	116	97	75	57
90% evap. @	166	153	149	128
FBP	206	199	194	182
Recovery, % vol	98.0	96.9	98.0	97.5
Residue, % vol	0.8	0.7	0.7	0.6
Loss, % vol	1.2	2.4	1.3	1.9
Phase Separation Temperature °C	<-40.0	-20.5	<-40.0	<-40.0

TABLE 25

BLENDING DATA FOR

REGULAR UNLEADED MOGAS/C_5 REACTOR EFFLUENT

Blend Composition % vol:				
Regular Unleaded	100.0	75.9	50.6	31.1
C_5 Reactor Effluent	0	24.1	49.4	68.9
Oxygen Content, % wt	Nil	1.0	2.0	3.0
Blend Research ON	94.2	95.2	95.6	96.2
Blend Motor ON	83.8	84.5	85.3	85.8
Delta Res ON over basefuel	0	1.0	1.4	2.0
Delta Motor ON over basefuel	0	0.7	1.5	2.0
Blending Res ON	0	98.4	97.0	97.1
Blending Motor ON	0	86.7	86.8	86.7
Blending Sensitivity	0	11.7	10.2	10.4
Reid Vapour Pressure, kPa	81.9	93.6	91.2	95.7
D867 Distillation, °C				
IBP	32	30	27	28
10% evap. @	53	41	37	35
50% evap. @	112	85	65	52
90% evap. @	181	172	158	131
FBP	216	213	202	194
Recovery, % vol	98.5	97.9	97.1	98.0
Residue, % vol	0.6	0.4	0.8	0.3
Loss, % vol	0.9	1.7	2.1	1.7
Phase Separation Temperature °C	<-40.0	-25.0	<-40.0	<-40.0

TABLE 26

BLENDING DATA FOR

PREMIUM UNLEADED MOGAS/50% TAME BLENDS (Partially Purified TAME)

Blend Composition % vol:				
Premium Unleaded Mogas	100.0	87.96	76.10	64.4
50% TAME Blends	0	12.04	23.90	35.6
Oxygen Content, % wt	Nil	1.0	2.0	3.0
Blend Research ON	96.2	96.7	97.6	97.4
Blend Motor ON	86.4	87.4	88.0	87.9
Delta Res ON over basefuel	0	0.5	1.4	1.2
Delta Motor ON over basefuel	0	1.0	1.6	1.5
Blending Res ON	0	100.4	102.1	99.6
Blending Motor ON	0	94.7	93.1	90.6
Blending Sensitivity	0	5.7	9.0	9.0
Reid Vapour Pressure, kPa	54.6	65.3	52.9	N/A
D867 Distillation, °C				
IBP	46	34	31	30
10% evap. @	78	58	51	51
50% evap. @	116	106	96	93
90% evap. @	166	161	154	152
FBP	206	199	193	191
Recovery, % vol	98.0	98.1	98.0	98.6
Residue, % vol	0.8	0.7	0.7	0.7
Loss, % vol	1.2	1.2	1.3	0.8
Phase Separation Temperature °C	<-40.0	-20.0	-27.5	N/A

N/A Result not available.

TABLE 27

BLENDING DATA FOR

REGULAR UNLEADED MOGAS/50% TAME BLENDS (Partially Purified TAME)

Blend Composition % vol:				
Regular Unleaded Mogas	100.0	88.12	76.3	64.7
50% TAME	0	11.88	23.7	35.3
Oxygen Content, % wt	Nil	1.0	2.0	3.0
Blend Research ON	94.2	94.8	95.8	96.7
Blend Motor ON	83.8	83.3	83.1	86.0
Delta Res ON over basefuel	0	0.6	1.6	2.5
Delta Motor ON over basefuel	0	-0.5	-0.7	2.2
Blending Res ON	0	99.3	101.0	101.3
Blending Motor ON	0	79.6	80.9	90.0
Blending Sensitivity	0	19.7	20.1	11.3
Reid Vapour Pressure, kPa	81.9	82.9	81.9	79.5
D867 Distillation, °C				
IBP	32	28	30	30
10% evap. @	53	47	44	44
50% evap. @	112	102	92	87
90% evap. @	181	176	172	166
FBP	216	214	211	207
Recovery, % vol	98.5	97.5	98.1	98.0
Residue, % vol	0.6	0.3	0.4	0.4
Loss, % vol	0.9	2.2	1.5	1.6
Phase Separation Temperature °C	<-40.0	-19.0	-28.5	<-40.0

TABLE 28

BUTANE DISPLACEMENT EFFECTS ON UNLEADED MOGAS/TAME BLENDS

Date in Tables 22 and 23 is summarized below as a function of RVP vs. l/v % nC_4 back in (or back out) using Figure 3.

% vol TAME		RVP kPa (psig)		RVP as l/v % nC_4	l/v of nC_4 Back In (Back Out)
Regular Unleaded	- 0	81.9	(11.9)	14.9	0
Regular Unleaded	+ 5.9%	78.8	(11.5)	14.0	+0.9
Regular Unleaded	+ 11.2%	75.7	(11.0)	12.9	+2.0
Regular Unleaded	+ 16.8%	70.1	(10.2)	11.2	+3.7
Premium Unleaded	- 0	54.6	(7.9)	6.3	0
Premium Unleaded	+ 6.0%	51.1	(7.4)	5.1	+1.2
Premium Unleaded	+ 11.3%	52.5	(7.6)	5.6	+0.7
Premium Unleaded	+ 16.2%	47.7	(6.9)	4.2	+2.1

Therefore, for a blend of unleaded mogas with 5-10% TAME, approximately 1% l/v additional n-butane can be added to either winter or summer grade to maintain RVP.

TABLE 29

COMPOSITIONAL ANALYSIS OF METHYL TERTIARY HEXYL ETHER FEEDSTOCK

(C_6 CATALYTICALLY CRACKED GASOLINE FRACTION 50-75°C)

Component	%, liquid volume
Isopentane	0.27
n-Pentane	0.35
Trans-2-Pentene	0.36
Cis-2-Pentene	0.23
Pentene-1	0.02
1,2-Pentadiene	0.07
2,3-Pentadiene	0.78
Cyclopentane	0.61
Cyclopentene	0.36
2,3-Dimethyl Butane	5.33
2-Methyl Pentane	26.6
3-Methyl Pentane	15.9
n-Hexane	4.68
C_6 Olefin	1.16
Trans-2-Hexene + 3-Methyl Cyclopentene	3.28
Cis-2-Hexene	1.40
Cis/Trans-3-Hexene	1.80
Hexene-1	0.90
Methyl Cyclopentane + 2,2-Dimethyl Pentane	11.2
Cyclohexane	0.31
Benzene	4.06
C_7^+	6.74
2-Methyl Butene-1*	0.07
2-Methyl Butene-2*	0.90
2-Methyl Pentene-1**	2.03
2-Methyl Pentene-2**	3.18
2-Ethyl Butene-1**	0.40
2,3-Dimethyl Butene-1**	0.61
2,3-Dimethyl Butene-2**	N.A.
Cis-3-Methyl Pentene-2**	2.31
Trans-3-Methyl Pentene-2**	2.87
1-Methyl Cyclopentene-1**	0.39
Total Liquid Volume %***	99.17

* TAME Reactive Olefin

** THME Reactive Olefin

*** Values computed from a Methyl Ethyl Ketone Internal Standard

TABLE 30

C_6 OPTIMIZATION EXPERIMENTS

Test Conditions	Feed	Run #1	Run #2	Run #3
Reactor Temperature (°C)	-	65	80	95
LHSV^{-h}	-	0.5	0.5	0.5
Reactor Pressure (mPa)	-	1.7	1.7	1.7
Methanol/Active Olefin Ratio (Molar)	-	1.04/1	1.04/1	1.04/1
Active C_4 (g/h)	N.D.	N.D.	N.D.	N.D.
Isobutene	N.D.	N.D.	N.D.	N.D.
Active C_5 (g/h)	0.51	0.25	0.26	0.38
2-Methyl Butene-1	0.02	0.04	0.03	0.07
2-Methyl Butene-2	0.49	0.21	0.23	0.31
Active C_6 (g/h)	3.45	2.06	2.09	2.43
2-Methyl Pentene-1	0.90	0.24	0.17	0.20
2-Methyl Pentene-2	0.80	0.68	0.78	1.01
2-Ethyl Butene-1	0.22	N.D.	N.D.	N.D.
Trans-3-Methyl Pentene-2	0.47	0.50	0.60	0.68
Cis-3-Methyl Pentene-2	0.59	0.44	0.45	0.47
2,3-Dimethyl Butene-1	0.36	0.11	0.06	0.05
2,3-Dimethyl Butene-2	N.A.	N.A.	N.A.	N.A.
1-Methyl Cyclopentene-1	0.11	0.09	0.03	0.02
Methanol (g/h)	1.61	0.20	0.49	0.56
Products (g/h)				
Dimethyl Ether	N.D.	0.03	0.10	0.26
MTBE	N.D.	N.D.	N.D.	N.D.
TAME	N.D.	0.82	0.46	0.29
Total THME	N.D.	(1.63)	(2.06)	(1.12)
2-Methyl-2-Methoxy Pentane	N.D.	1.05	1.26	0.78
3-Methyl-3-Methoxy Pentane	N.D.	0.38	0.40	0.21
2,3 Dimethyl-2 Methoxy Pentane	N.D.	0.16	0.36	0.10
1-Methyl-1-Methoxy Cyclopentane	N.D.	0.04	0.04	0.03
Elemental Analysis				
Nitrogen, ppm w/w as N	6.6	2.9	4.5	3.3
Sulfur, ppm w/w as S	30	20	50	20
Oxygen, % w/w as O_2	-	1.4	1.9	1.7
Gravity kg/L @ 15°C	0.6786	0.6709	0.6824	0.6819
Mass Balance				
Based upon Total Feed	-	97.5	98.7	100.0
Based on Total Active C_6	-	93.9	104.1	93.9
Based on Total Methanol Consumption	-	59.0	83.2	82.0
Conversion				
Based on Total Active C_6	-	40.3	39.4	35.4
Based on THME Present	-	34.3	43.3	23.6

N.D. = Not Detected
N.A. = Not Available

TABLE 31

C_6 OPTIMIZATION EXPERIMENTS

Test Conditions	Feed	Run #4	Run #5	Run #6
Reactor Temperature (°C)	-	65	80	95
LHSV-h	-	2.0	2.0	2.0
Reactor Pressure (mPa)	-	1.7	1.7	1.7
Methanol/Active Olefin Ratio (Molar)	-	1.04/1	1.04/1	1.04/1
Active C_4 (g/h)	N.D.	N.D.	N.D.	N.D.
Isobutene	N.D.	N.D.	N.D.	N.D.
Active C_5 (g/h)	2.04	1.49	1.10	0.80
2-Methyl Butene-1	0.09	0.07	0.08	0.12
2-Methyl Butene-2	1.95	1.42	1.02	0.78
Active C_6 (g/h)	13.86	11.11	9.20	9.12
2-Methyl Pentene-1	3.62	2.43	1.38	0.90
2-Methyl Pentene-2	3.22	3.49	3.00	3.38
2-Ethyl Butene-1	0.87	N.D.	N.D.	N.D.
Trans-3-Methyl Pentene-2	1.89	1.84	2.09	2.49
Cis-3-Methyl Pentene-2	2.37	2.15	1.99	1.92
2,3-Dimethyl Butene-1	1.46	1.04	0.62	0.33
2,3-Dimethyl Butene-2	N.A.	N.A.	N.A.	N.A.
1-Methyl Cyclopentene-1	0.43	0.16	0.12	0.10
Methanol (g/h)	6.43	4.91	4.12	3.88
Products (g/h)				
Dimethyl Ether	N.D.	N.D.	0.10	0.30
MTBE	N.D.	N.D.	N.D.	N.D.
TAME	N.D.	0.81	1.49	1.42
Total THME	N.D.	(3.58)	(6.18)	(5.80)
2-Methyl-2-Methoxy Pentane	N.D.	2.03	3.88	3.92
3-Methyl-3-Methoxy Pentane	N.D.	0.97	1.48	1.18
2,3 Dimethyl-2-Methoxy Pentane	N.D.	0.35	0.61	0.55
1-Methyl-1-Methoxy Cyclopentane	N.D.	0.23	0.21	0.15
Elemental Analysis				
Nitrogen, ppm w/w as N	6.6	5.5	6.1	4.6
Sulfur, ppm w/w as S	30	40	30	40
Oxygen, % w/w as O_2	-	2.3	2.3	2.3
Gravity kg/L @ 15°C	0.6786	0.6806	0.6830	0.6829
Mass Balance				
Based upon Total Feed	-	100.3	98.1	98.4
Based on Total Active C_6	-	98.9	98.8	96.2
Based on Total Methanol Consumption	-	95.6	100.0	99.1
Conversion				
Based on Total Active C_6	-	19.8	33.6	34.2
Based on THME Present	-	18.8	32.4	30.4

N.D. = Not Detected
N.A. = Not Available

TABLE 32

C_6 OPTIMIZATION EXPERIMENTS

	Feed	Run #7	Run #8	Run #9	
Test Conditions					
Reactor Temperature (°C)	-	65	80	95	
LHSV-h	-	0.5	0.5	0.5	
Reactor Pressure (mPa)	-	1.7	1.7	1.7	
Methanol/Active Olefin Ratio (Molar)	-	0.77/1	0.77/1	0.77/1	
Active C_4 (g/h)	N.D.	N.D.	N.D.	N.D.	
Isobutene	N.D.	N.D.	N.D.	N.D.	
Active C_5 (g/h)	0.37	0.17	0.29	0.36	
2-Methyl Butene-1	0.02	0.01	0.02	0.10	
2-Methyl Butene-2	0.35	0.16	0.27	0.26	
Active C_6 (g/h)	3.66	2.81	2.50	3.34	
2-Methyl Pentene-1	0.69	0.39	0.31	0.22	
2-Methyl Pentene-2	0.94	0.91	0.86	1.15	
2-Ethyl Butene-1	0.16	N.D.	N.D.	0.20	
Trans-3-Methyl Pentene-2	0.80	0.87	0.67	1.03	
Cis-3-Methyl Pentene-2	0.69	0.57	0.54	0.68	
2,3-Dimethyl Butene-1	0.23	0.10	0.12	0.06	
2,3-Dimethyl Butene-2	N.A.	N.A.	N.A.	N.A.	
1-Methyl Cyclopentene-1	0.15	0.07	N.D.	N.A.	
Methanol (g/h)	1.20	0.72	0.78	0.47	
Products (g/h)					
Dimethyl Ether	N.D.	0.02	0.06	0.24	
MTBE	N.D.	N.D.	N.D.	N.D.	
TAME	N.D.	0.42	0.33	0.19	
Total THME	N.D.	(1.21)	(1.47)	(1.00)	
2-Methyl-2-Methoxy Pentane	N.D.	0.74	0.93	0.63	
3-Methyl-3-Methoxy Pentane	N.D.	0.30	0.35	0.23	
2,3 Dimethyl-2-Methoxy Pentane	N.D.	0.10	0.13	0.07	
1-Methyl-1-Methoxy Cyclopentane	N.D.	0.07	0.06	0.07	
Elemental Analysis					
Nitrogen, ppm w/w as N	7.0	6.8	5.4	3.0	
Sulfur, ppm w/w as S	33	150	150	130	
Oxygen, % w/w as O_2	-	1.7	1.9	1.4	
Gravity kg/L @ 15°C	0.6842	0.6929	0.6918	0.6911	
Mass Balance					
Based upon Total Feed	-	100.9	100.1	98.2	
Based on Total Active C_6	-	102.2	97.5	111.2	
Based on Total Methanol Consumption	-	100.8	114.2	95.0	
Conversion					
Based on Total Active C_6	-	23.2	31.7	8.7	
Based on THME Present	-	24.0	29.2	19.8	

N.D. = Not Detected
N.A. = Not Available

TABLE 33

C_6 OPTIMIZATION EXPERIMENTS

Test Conditions	Feed	Run #10	Run #11	Run #12	
Reactor Temperature (°C)	-	65	80	95	
LHSV-h	-	2.0	2.0	2.0	
Reactor Pressure (mPa)	-	1.7	1.7	1.7	
Methanol/Active Olefin Ratio (Molar)	-	0.77/1	0.77/1	0.77/1	
Active C_4 (g/h)	N.D.	N.D.	N.D.	N.D.	
Isobutene	N.D.	N.D.	N.D.	N.D.	
Active C_5 (g/h)	1.50	1.57	1.22	1.23	
2-Methyl Butene-1	0.08	0.37	0.24	0.27	
2-Methyl Butene-2	1.42	1.20	0.98	0.96	
Active C_6 (g/h)	14.63	12.79	11.82	11.98	
2-Methyl Pentene-1	2.73	2.17	1.57	1.10	
2-Methyl Pentene-2	3.75	3.75	3.64	4.09	
2-Ethyl Butene-1	0.66	N.D.	N.D.	N.D	
Trans-3-Methyl Pentene-2	3.22	3.30	3.38	3.82	
Cis-3-Methyl Pentene-2	2.77	2.80	2.66	2.62	
2,3-Dimethyl Butene-1	0.90	0.77	0.57	0.35	
2,3-Dimethyl Butene-2	N.A.	N.A.	N.A.	N.A.	
1-Methyl Cyclopentene-1	0.60	N.D.	N.D.	N.D.	
Methanol (g/h)	4.81	2.10	1.56	1.29	
Products (g/h)					
Dimethyl Ether	N.D.	N.D.	0.07	0.27	
MTBE	N.D.	N.D.	N.D.	N.D.	
TAME	N.A.	0.57	0.90	0.81	
Total THME	N.D.	(4.43)	(5.10)	(4.48)	
2-Methyl-2-Methoxy Pentane	-	2.50	2.75	2.72	
3-Methyl-3-Methoxy Pentane	-	1.09	1.44	1.08	
2,3-Dimethyl-2-Methoxy Pentane	-	0.24	0.37	0.34	
1-Methyl-1-Methoxy Cyclopentane	-	0.60	0.54	0.34	
Elemental Analysis					
Nitrogen, ppm w/w as N	7.0	5.1	5.2	4.4	
Sulfur, ppm w/w as S	33	160	150	130	
Oxygen, % w/w as O_2	-	1.3	1.2	1.1	
Gravity kg/L @ 15°C	0.6842	0.6895	0.6904	0.6902	
Mass Balance					
Based upon Total Feed	-	98.7	98.8	97.8	
Based on Total Active C_6	-	109.4	106.1	104.1	
Based on Total Methanol Consumption	-	72.8	69.6	61.7	
Conversion					
Based on Total Active C_6	-	12.6	19.2	18.1	
Based on THME Present	-	22.0	25.3	22.2	

N.D. = Not Detected
N.A. = Not Available

TABLE 34

THME PRODUCTION RUN DATA

Test Conditions	Feed #1	Product #1	Feed #2	Product #2	Feed #3	Product #3	Average Feed Values	Composite Sample (Total Product)
Reactor Temperature (°C)	-	80	-	80	-	80	-	80
LHSV-h	-	0.5	-	0.5	-	0.5		0.5
Reactor Pressure (mPa)	-	1.7	-	1.7	-	1.7	-	1.7
Methanol/Active Olefin Ratio (Molar)	-	0.97	-	0.97	-	1.07/1	-	0.99/1
Active C4 (g/h)								
Isobutene	-	-	-	-	-	-	-	-
Active C_5 (g/h)	(3.78)	(1.71)	(3.34)	(1.61)	(2.18)	(1.68)	(3.10)	(1.61)
2-Methyl Butene-1	0.25	0.17	0.20	0.16	0.28	0.16	0.24	0.09
2-Methyl Butene-2	3.53	1.54	3.14	1.45	1.91	1.42	2.86	1.52
Active C_6 (g/h)	(39.51)	(25.30)	(39.30)	(24.82)	(39.10)	(24.88)	(39.31)	(25.33)
2-Methyl Pentene-1	6.69	1.48	6.69	1.54	6.63	1.57	6.67	1.60
2-Methyl Pentene-2	10.53	7.70	10.48	7.57	10.44	7.61	10.48	7.76
2-Ethyl Butene-1	1.38	N.D.	1.29	N.D.	1.31	N.D.	1.33	N.D.
Trans-3-Methyl Pentene-2	9.60	9.22	9.67	8.97	9.64	8.86	9.64	9.13
Cis-3-Methyl Pentane-2	7.80	6.12	7.75	6.01	7.72	6.02	7.76	6.11
2,3-Dimethyl Butene-2	2.04	0.47	2.01	0.49	1.96	0.52	2.00	0.51
2-Ethyl Butene-2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
1-Methyl Cyclopentene-1	1.47	0.31	1.41	0.24	1.40	0.30	1.43	0.22
Methanol (g/h)	16.19	6.61	15.92	7.29	16.36	7.68	15.92	6.42
Products (g/h)								
Dimethyl Ether	N.D.	0.96	N.D.	0.83	N.D.	0.84	N.D.	0.72
MTBE	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
TAME	N.D.	3.33	N.D.	3.07	N.D.	3.14	N.D.	3.19
Total THME	N.D.	(23.10)	N.D.	(22.09)	N.D.	(21.37)	N.D.	(22.12)
2-Methyl-2 Methoxy Pentane		6.46	-	6.25	-	6.07	-	6.28
3-Methyl-3 Methoxy Pentane		12.94	-	12.25	-	11.79	-	12.21
2,3-Dimethyl-2 Methoxy Pentane		1.73	-	1.65	-	1.60	-	1.68
1-Methyl-1-Methoxy Cyclopentane		1.97	-	1.94	-	1.91	-	1.95
Elemental Analysis								
Nitrogen, ppm w/w as N	7.0	-	7.0	-	7.0	-	-	7.0
Sulfur, ppm w/w as S	3.3	-	3.3	-	3.3	-	-	3.3
Oxygen, % w/w as O_2	N.D.	2.2	-	2.2	-	2.2	-	2.1
Gravity kg/L @ 15°C	0.6842	-	0.6842	-	0.6842	-	0.6842	0.6824
Mass Balance								
Based upon Total Feed	-	99.0	-	99.9	-	101.1	-	99.8
Based on Active C_6	-	106.4	-	103.9	-	107.1	-	105.3
Based on Methanol Consumption	-	88.7	-	97.4	-	96.2	-	91.2
Conversion								
Based on Total Active C_6	-	36.0	-	36.8	-	34.0	-	35.6
Based on THME Present	-	42.4	-	40.8	-	41.1	-	40.8

N.D. = Not Detected
N.A. = Not Available

TABLE 35

COMPOSITIONAL ANALYSIS OF THME FEED AND PRODUCT

Component	Feed (% Liq Vol)	Final Product (% Liq Vol)
Isobutane	0.26	0.37
Pentene-1	0.02	0.03
2-Methyl Butene-1	0.07	0.03
n-Pentane	0.34	0.40
Trans-2-Pentene	0.35	0.40
Cis-2-Butene	0.22	0.24
2-Methyl Butene-2	0.86	0.45
1,2-Pentadiene	0.07	0.07
Cyclopentene	0.35	0.32
2,3-Pentadiene	0.75	0.79
Cyclopentane	0.59	0.56
2,3-Dimethyl Butane	5.12	5.55
2-Methyl Pentane	25.5	25.6
C_6 Olefin	1.11	1.11
3-Methyl Pentene	15.2	16.3
Hexene-1	0.86	0.90
n-Hexane	4.49	4.28
Cis & Trans Hexene-3	1.73	1.81
3 Methyl Cyclopentene + Trans-2-Hexene	3.15	3.29
Cis-Hexene-2	1.34	1.41
Methyl Cyclopentane + 2,2 Dimethyl Pentane	10.7	10.2
2,4-Dimethyl Pentane	1.52	1.76
Benzene	3.90	3.85
Cyclohexane	0.30	0.27
C_7+	4.95	4.85
MTBE	N.D.	N.D.
TAME	N.D.	0.83
Total THME	N.D.	(5.67)
2-Methyl-2-Methoxy Pentane	N.D.	1.61
3-Methyl-3-Methoxy Pentane	N.D.	3.13
2,3-Dimethyl-2-Methoxy Butane	N.D.	0.43
1-Methyl-1-Methoxy Cyclopentane	N.D.	0.50
2-Methyl-Pentene-1	1.95	0.47
2-Methyl-Pentene-2	3.05	2.26
2-Ethyl-Butene-1	0.38	N.D.
2,3-Dimethyl Butene-1	0.59	0.15
2,3-Dimethyl Butene-2	N.D.	N.A
Cis-3-Methyl Pentene-2	2.22	1.75
Trans-3-Methyl Pentene-2	2.75	2.60
1-Methyl Cyclopentene-1	0.37	0.04
Methanol	4.02	1.62
Dimethyl Ether	N.D.	0.20

N.D. = Not detected
N.D. = Not available

TABLE 36

SEPARATION OF METHANOL, THME AND UNREACTED HYDROCARBON

Distillation	% Distilled (Liq Vol)	Methanol (% Liq Vol)	THME (% Liq Vol)	Hydrocarbon (% Liq Vol)
IBP - 64°C	58.7	1.5	N.D.	98.5
64 - 66°C	16.0	N.D.	N.D.	100.0
66 - 108°C	20.9	N.D.	2.1	97.9
108°C	3.4	N.D.	90.0	10.0
Loss	1.0	-	-	-
Feed	-	1.4	3.7	94.9

Boiling Points - Methanol = 65°C
THME = 106-114°C

Glycol Extraction

	0.5M Glycol* % by wt			0.25M Glycol* % by wt			0.125M Glycol* % by wt		
	Methanol	THME	HC**	Methanol	THME	HC**	Methanol	THME	HC**
Feed	1.36 _	4.0	94.6	1.36	4.0	94.6	1.36	4.0	94.6
Product	N.D.	4.0	96.0	0.04	4.0	96.0	0.05	4.0	95.9

* 0.5M, 025M and 0.125M molar ratios of Glycol/Reactor product were separately extracted

** HC = Hydrocarbon

TABLE 36 Continued

SEPARATION OF METHANOL, THME AND UNREACTED HYDROCARBON

Molecular Sieve Adsorption

Sieve Type		= 4a
Mesh Size		= 40 - 60 mesh
Adsorber Dimensions		
	Height	= 25 cm
	Diameter	= 0.8 cm
	Volume	= 12.56 mL
Wt of Sieve		= 11.0 g
Flow Rate		= 0.32 mL/min
Contact Time		= 39.3 min
Temperature		= 23°C

Volume Processed (mL)	Methanol (% Liq Vol)	THME (% Liq Vol)	Hydrocarbon (% Liq Vol)
30	N.D.	3.8	96.2
60	0.22	3.6	96.2
120	0.27	3.7	96.0
200	0.59	3.6	95.8
280	0.85	3.6	95.5
360	1.03	3.7	95.3
500	1.01	3.6	95.4
570	1.05	3.7	95.3
Feed	1.20	3.5	95.3

TABLE 37

METHANOL SEPARATION - C6 RECYCLE EXPERIMENT

Parameter	Feed		Run #1	
Test Conditions				
Reactor Temperature (°C)	-		80	
$LHSV^{-h}$	-		0.5	
Reactor Pressure (mPa)	-		250	
Methanol/Active Olefin Ratio (Molar)	-		Recycle	
Active C_4 (g/h)	-		-	
Isobutene		-		-
Active C_5 (g/h)	0.29		0.19	
2-Methyl Butene-1		0.02		0.01
2-Methyl Butene-2		0.27		0.18
Active C_6 (g/h)	(2.55)		(2.14)	
2-Methyl Pentene-1		0.31		0.15
2-Methyl Pentene-2		0.86		0.69
2-Ethyl Butene-1		N.D.		N.D.
Trans-3-Methyl Pentene-2		0.67		0.74
Cis-3-Methyl Pentene-2		0.54		0.51
2,3-Dimethyl Butene-1		0.12		0.05
2,3-Dimethyl Butene-2		N.A.		N.A.
1-Methyl Cyclopentene-2		0.05		N.D.
Methanol (g/h)		0.55		0.34
Products (g/h)				
Dimethyl Ether		0.06		0.11
MTBE		N.D.		N.D.
TAME		0.33		0.35
Total THME		(1.46)		(1.88)
2 Methyl-2-Methoxy Pentane		0.35		0.47
3 Methyl-3-Methoxy Pentane		0.92		1.14
2,3-Dimethyl-2-Methoxy Butane		0.13		0.15
1 Methyl=1-Methoxy Cyclopentane		0.06		0.12
Elemental Analysis				
Nitrogen, ppm w/w as N		-		-
Sulfur, ppm w/w as S		-		-
Oxygen, % w/w as O_2		-		-
Gravity kg/L @ 15°C		-		-
Mass Balance				
Based upon Total Feed		-		100.0
Based on Active C_6		-		96.1
Based on Methanol Consumption		-		105.0
Conversion				
Based on Active C_6		-		16.5
Based on THME		-		12.0

N.D. = Not Detected

TABLE 38

BLENDING DATA FOR

PREMIUM UNLEADED MOGAS/PURE C_6 ETHER (THME) BLENDS

Blend Composition % vol:			
Premium Unleaded	100.0	97.21	94.09
Pure C_6 (THME) Ether	0	2.79	5.91
Oxygen Content, % wt	0	0.50	1.0
Blend Research ON	96.2	96.0	96.0
Blend Motor ON	86.4	86.3	86.2
Delta Res ON over basefuel	0	-0.2	-0.2
Delta Motor ON over basefuel	0	-0.1	-0.2
Blending Res ON	0	89.0	92.8
Blending Motor ON	0	82.8	83.0
Blending Sensitivity	0	6.2	9.8
Reid Vapour Pressure, kPa	54.6	50.8	50.8
D867 Distillation, °C			
IBP	46	37	34
10% evap. @	78	67	70
50% evap. @	116	114	115
90% evap. @	166	165	165
FBP	206	200	209
Recovery, % vol	98.0	98.1	98.5
Residue, % vol	0.8	0.8	0.4
Loss, % vol	1.2	1.1	1.1
Phase Separation Temperature °C	<-40.0	-16.5	-11.5

TABLE 39

BLENDING DATA FOR

REGULAR UNLEADED MOGAS/PURE C_6 ETHER (THME) BLENDS

Blend Composition % vol:			
Regular Unleaded	100.0	97.25	94.16
Pure C_6 (THME) Ether	0	2.75	5.84
Oxygen Content, % wt	0	0.50	1.0
Blend Research ON	94.2	94.0	94.2
Blend Motor ON	83.8	83.3	83.1
Delta Res ON over basefuel	0	-0.2	0.0
Delta Motor ON over basefuel	0	-0.5	-0.7
Blending Res ON	0	86.9	94.2
Blending Motor ON	0	65.6	71.8
Blending Sensitivity	0	21.3	22.4
Reid Vapour Pressure, kPa	81.9	76.0	73.6
D867 Distillation, °C			
IBP	32	31	32
10% evap. @	53	48	50
50% evap. @	112	109	111
90% evap. @	181	178	179
FBP	216	214	217
Recovery, % vol	98.5	97.4	97.5
Residue, % vol	0.6	0.6	0.5
Loss, % vol	0.9	2.0	2.0
Phase Separation Temperature °C	-40.0	-12.5	- 8.5

TABLE 40

BLENDING DATA FOR

PREMIUM UNLEADED MOGAS/PURE C_6 REACTOR EFFLUENT BLENDS

Blend Composition % vol:			
Premium Unleaded	100.0	53.2	9.80
C_6 Reactor Effluent	0	46.8	90.20
Oxygen Content, % wt	0	1.0	2.0
Blend Research ON	96.2	92.7	89.7
Blend Motor ON	86.4	84.2	81.2
Delta Res ON over basefuel	0	-3.5	-6.5
Delta Motor ON over basefuel	0	-2.2	-5.2
Blending Res ON	0	88.7	89.0
Blending Motor ON	0	81.7	80.6
Blending Sensitivity	0	7.0	8.4
Reid Vapour Pressure, kPa	54.6	58.4	55.3
D867 Distillation, °C			
IBP	46	41	47
10% evap. @	78	62	57
50% evap. @	116	84	68
90% evap. @	166	149	92
FBP	206	192	154
Recovery, % vol	98.0	98.9	98.4
Residue, % vol	0.8	0.8	0.8
Loss, % vol	1.2	0.3	0.8
Phase Separation Temperature °C	<-40.0	<-40.0	<-40.0

TABLE 41

BLENDING DATA FOR

REGULAR UNLEADED MOGAS/PURE C_6 REACTOR EFFLUENT BLENDS

Blend Composition % vol:			
Regular Unleaded	100.0	53.5	10.0
C_6 Reactor Effluent	0	46.5	90.0
Oxygen Content, % wt	0	1.0	2.0
Blend Research ON	94.2	91.9	89.3
Blend Motor ON	83.8	82.2	81.1
Delta Res ON over basefuel	0	-2.3	-4.9
Delta Motor ON over basefuel	0	-1.6	-2.7
Blending Res ON	0	89.3	88.8
Blending Motor ON	0	80.4	80.8
Blending Sensitivity	0	8.9	8.0
Reid Vapour Pressure, kPa	81.9	68.1	56.3
D867 Distillation, °C			
IBP	32	33	45
10% evap. @	53	51	56
50% evap. @	112	77	67
90% evap. @	181	158	88
FBP	216	206	168
Recovery, % vol	98.5	99.0	99.0
Residue, % vol	0.6	0.4	0.7
Loss, % vol	0.9	0.6	0.3
Phase Separation Temperature °C	<-40.0	<-40.0	<-40.0

TABLE 42

THME AND RELATED OCTANE BLENDING VALUES

COMPONENT	RON	MON
THME	90.0	82.0
C_6 Olefin Feed Stream	92.5	80.6
C_6 Reactor Product	92.5	81.6
C_6 Unreacted Hydrocarbons	90.9	79.8
1-Methyl Cyclopentene -1	90.3	72.0
2-Methyl Pentene-1	94.2	81.5
2-Methyl Pentene-2	97.8	83.0
Cis-3-Methyl Pentene-2	N.A.	N.A.
Trans-3-Methyl Pentene-2	97.2	81.0
2-Ethyl Butene-1	98.3	79.4
2,3-Dimethyl Butene-1	100.1	82.8
2,3-Dimethyl Butene-2	97.4	80.5

N.A. = not available

TABLE 43

BUTANE DISPLACEMENT EFFECTS ON UNLEADED MOGAS/THME BLENDS

Date in Tables 38 and 39 is summarized below as a function of RVP vs. l/v % nC_4 back in (or back out) using Figure 3.

% vol THME		RVP kPa (psig)		RVP as l/v % nC_4	l/v of nC_4 Back In (Back Out)
Regular Unleaded	- 0	81.9	(11.9)	14.9	0
Regular Unleaded	+ 2.75%	76.0	(11.0)	12.7	+2.2
Regular Unleaded	+ 5.84%	73.6	(10.7)	12.3	+2.6
Premium Unleaded	- 0	54.6	(7.9)	6.3	0
Premium Unleaded	+ 2.79%	50.8	(7.4)	4.7	+1.6
Premium Unleaded	+ 5.91%	50.8	(7.4)	4.7	+1.6

Therefore, for a blend of unleaded mogas with 5-10% THME, approximately 1.5% l/v additional n-butane can be added to either winter or summer grade to maintain RVP.

TABLE 44

ECONOMIC PREDICTIONS
(% of Gross Income)

	Savings Over Base Case I (% of Gross Income)	Savings Over Base Case II (% of Gross Income)
MTBE Plant, Lead and MMT Allowed	-0.025	-
TAME Plant, Lead and MMT Allowed	+0.04	-
MTBE + TAME, Lead and MMT Allowed	-0.03	-
Isomerization Processing, No Lead or MMT Allowed	+0.52	-
MTBE Plant + Isomerization Processing, No lead or MMT Allowed	-	-0.05
TAME Plant + Isomerization Processing, No Lead or MMT Allowed	-	-0.02
MTBE + TAME PLants + Isomerization Processing, No Lead or MMT Allowed	-	-0.046

Base Case I - Refinery as is, no additional processing, lead and MMT allowed

Base Case II - Isomerization Processing added, lead and MMT not allowed

Capital Costs

MTBE Plant = $2,500,000
TAME Plant = $500,000
Isomerization Plant = $18,000,000

TABLE 45

REFINERY GASOLINE PROCESSING VOLUMES
(Octane - $m^3/a \times 1 \times 10^6$)

Volume Octane - $m^3 \times 1 \times 10^6/a$	Base Case I				Base Case II			
	Base Case I	MTBE Plant	TAME Plant	MTBE + TAME Plant	Base Case II	MTBE Plant	TAME Plant	MTBE + TAME Plant
MTBE	-	2.7	-	2.7	-	2.6	-	1.2
Alkylate	33.0	26.3	32.8	26.3	32.8	25.7	32.7	29.4
MTBE Octane Contribution	-	-4.0	-	-4.0	-	-4.5	-	-2.2
C_5 Ex TAME Process	-	-	16.1	16.1	-	-	16.1	16.1
FCCU Gasoline	93.3	93.0	78.2	77.9	93.3	92.5	77.8	77.9
TAME Octane Contribution	-	-	+1.0	+0.7	-	-	+0.7	+0.7
DiH Overheads (mixed C_5/C_6)	25.3	26.3	25.5	26.3	-	-	-	-
Isomerate	-	-	-	-	30.4	32.2	30.5	31.8
Isomerate Contribution	-	-	-	-	+5.1	+6.9	+5.2	+6.5
Platformate	33.1	35.0	33.5	35.2	32.0	34.1	32.2	33.1
Reformate	22.5	23.2	27.5	23.3	23.2	24.5	23.2	23.9
Butane	28.4	28.4	27.4	27.4	27.4	27.3	26.4	26.3
Anti-knock Additive	3.7	4.4	3.2	4.1	-	-	-	-
TOTAL	239.3	239.3	239.2	239.3	239.1	238.9	239.0	239.7

Base Case I - TEL and MMT allowed, no isomerization processing
Base Case II - TEL and MMT not allowed, isomerization processing utilized

Octane - m^3 = Calculated Octane Road Index X Volume of Gasoline Blending Component
Anti-knock Volume = Octane Blending Requirement X Total Volume of Gasoline Pool

TABLE 46

REFINERY GASOLINE PROCESSING VOLUMES
(1 X 10^6 m^3/a)

Volume 1 X 10^6 m3/a	Base Case I				Base Case II			
	Base Case I	MTBE Plant	TAME Plant	MTBE + TAME Plant	Base Case II	MTBE Plant	TAME Plant	MTBE + TAME Plant
MTBE	-	0.0250	-	0.0250	-	0.0243	-	0.0114
Alkylate	0.359	0.287	0.357	0.287	0.357	0.280	0.356	0.320
C_5 Ex TAME Process	-	-	0.177	0.177	-	-	0.177	0.177
FCCU Gasoline	1.060	1.054	0.888	0.880	1.059	1.049	0.888	0.884
DiH Overheads (C_5/C_6 mix)	0.340	0.354	0.343	0.354	-	-	-	-
Isomerate	-	-	-	-	0.334	0.353	0.335	0.344
Platformate	0.351	0.372	0.355	0.375	0.352	0.374	0.353	0.363
Reformate	0.259	0.279	0.260	0.280	0.279	0.301	0.283	0.292
Butane	0.299	0.299	0.289	0.289	0.288	0.287	0.278	0.277
Total Volume	2.668	2.670	2.669	2.667	2.669	2.668	2.670	2.668

Base Case I - TEL and MMT allowed, no isomerization processing
Base Case II - TEL and MMT not allowed, isomerization processing utilized

TABLE 47

ALKYLATION UNIT FEED
m^3/SD

	Base Case I	MTBE Plant	TAME Plant	MTBE + TAME Plant	Base Case II	MTBE Plant	TAME Plant	MTBE + TAME Plant	Percent of Feed
n-Butane	62.0	49.4	61.7	49.4	62.5	50.0	62.3	56.0	4.8
Insobutane	630	503	627	503	636	498	634	570	48.9
Propylenes	200	160	199	160	202	158	202	181	15.5
FCC Propane	85.9	68.5	85.5	68.5	86.6	67.9	86.5	77.6	6.7
Butenes*	311	-	310	-	314	-	313	-	24.1
Butenes ex MTBE Unit	-	248	-	248	-	246	-	281	(24.1)
Total Alkylation Feed	1289	1029	1283	1029	1301	1020	1298	1116	-

Note:

*The data given in this table is intended to show the effect of the reduced isobutene concentration upon field butane purchase for alkylation feed. The isobutene content of the mixed butylenes ranges from 22-25%. The isobutene content of the C_4 FCC hydrocarbons (mixed butenes + FCC non-purchased butanes) is 11-12%.

TABLE 48

PROCESS UNIT TOTAL PRODUCT EFFLUENT
m^3/SD

	Base Case I	MTBE Plant	TAME Plant	MTBE + TAME Plant	Base Case II	MTBE Plant	TAME Plant	MTBE + TAME Plant
Crude Unit	14,716	14,710	14,712	14,704	14,605	14,633	14,587	14,600
FCC Unit	4,677	4,677	4,677	4,677	4,677	4,677	4,677	4,677
Alkylation Unit	983	785	979	785	922	778	990	943
Platformer	1,217	1,289	1,232	1,294	1,140	1,216	1,144	1,180
Reformer	976	1,006	978	1,010	946	1,045	949	975
MTBE Plant (Pure MTBE)	-	68	-	68	-	68	-	32
TAME Plant (C_5 Reactor Effluent)	-	-	488	488	-	-	488	488
DiH Overheads (Isomerization Feed)	937	973	944	975	-	-	-	-
Isomerization Plant	-	-	-	-	897	952	899	926

Unit Capacity m^3/SD

Crude Unit	=	16,000
FCC Unit	=	4,800
Reformer	=	3,500
Alkylation	=	1,000
Isomerization	=	1,000

TABLE 49

CRUDE AND RAW MATERIAL PURCHASE
m^3/SD

	Base Case I				Base Case II			
	Base Case I	MTBE Plant	TAME Plant	MTBE + TAME Plant	Base Case II	MTBE Plant	TAME Plant	MTBE + TAME Plant
Syncrude	2,800	2,800	2,800	2,800	2,800	2,800	2,800	2,800
B.C. Light Crude	2,160	1,082	1,995	1,082	2,534	776	2,442	1,594
Peace River Crude	8,900	10,113	9,093	10,137	8,400	10,359	8,502	9,448
Field Butane	860	713	825	685	872	697	842	715
Natural Gas	16	15	14	15	69	32	72	54
Methanol	-	26	20	46	-	26	20	33
TOTAL	14,736	14,749	14,747	14,765	14,675	14,690	14,678	14,644

Base Case I - TEL and MMT allowed, no isomerization processing
Base Case II - Tel and MMT not allowed, isomerization processing utilized

TABLE 50

RAW MATERIAL COSTS

	C/L
Syncrude	11.94
B.C. Light Crude	12.09
Peace River Crude	12.09
Field Butane	10.28
Natural Gas	8.74
Methanol	9.48

Source: Cooperate Survey, May 1987

TABLE 51

REFINERY PRODUCTS

Product	m^3/CD
Super Unleaded Gasoline	1460
Regular Unleaded Gasoline	5110
Regular Leaded Gasoline	730
Jet B Fuel	150
Jet A Fuel	810
Stove Oil	90
Diesel 25	2772
Diesel 20X	1848
Bunker	1116
Propane (HD-5)	315
Refinery Fuel Gas	500

TABLE 52

PREMIUM UNLEADED GASOLINE BLENDS
m^3/CD

	Base Case I	MTBE Plant	TAME Plant	MTBE + TAME Plant	Base Case II	MTBE Plant	TAME Plant	MTBE + TAME Plant	Specification Max	Specification Min
n-Butane	172	181	172	164	165	159	152	145	-	-
DiH Overheads	26.6	41.2	26.6	155	-	-	-	-	-	-
Reformate	246	288	248	-	-	-	-	-	-	-
Platformate	33.9	166	36	357	64.9	-	-	-	-	-
Alkylate	983	785	979	785	992	778	990	890	-	-
FCC Gasoline	-	-	-	-	239	472	148	123	-	-
MTBE	-	-	-	-	-	52.3	-	-	-	-
C_5 ex TAME Process	-	-	-	-	-	-	172	304	-	-
Reid Vapour Pressure	233	233	233	233	233	233	233	233	233	176
% Evaporated @ 82°C	34.0	33.2	34.0	33.2	32.3	33.8	34.2	35.2	50.0	-
% Evaporated @ 112°C	68.8	65.7	68.8	61.1	64.6	64.7	66.6	66.5	-	50.0
Calc. Road O.N.	91.8	91.8	91.8	91.8	91.8	91.8	91.8	91.8	-	91.8
MMT g/L as Mn	0.005	0.005	0.005	0.005	0	0	0	0	<0.018* 0**	-

Note:

* Base Case I = <0.018 g/L manganese
**Base Case II = 0.0 g/L manganese

TABLE 53

REGULAR UNLEADED GASOLINE BLENDS
m^3/CD

	Base Case I				Base Case II				Specification	
	Base Case I	MTBE Plant	TAME Plant	MTBE + TAME Plant	Base Case II	MTBE Plant	TAME Plant	MTBE + TAME Plant	Max	Min
n-Butane	563	549	534	537	515	515	500	504	-	-
DiH Overheads (C_5/C_6 mix)	718	756	724	643	-	-	-	-	-	-
Reformate	-	-	-	290	126	180	129	153	-	-
Platformate	928	852	937	670	913	1049	988	1021	-	-
Isomerate	-	-	-	-	889	945	892	919	-	-
MTBE	-	68.4	-	68.4	-	15.4	-	31.6	-	-
C_5 ex TAME Process	-	-	484	484	-	-	312	179	-	-
FCCU Gasoline	2904	2888	2434	2420	2671	2411	2292	2305	-	-
Reid Vapour Pressure	233	233	233	233	233	233	233	233	233	176
% Evaporated @ 82°C	39.3	39.8	39.9	40.4	40.7	40.7	40.9	40.8	50.0	-
% Evaporated @ 112°C	59.0	59.8	59.6	61.7	61.0	61.0	61.1	61.1	-	50.0
MON	83.6	83.6	83.7	83.7	84.3	84.4	84.3	84.4	-	82.0
Calc. Road O.N.	89.0	89.0	89.0	89.0	89.0	89.0	89.0	89.0	-	89.0
MMT g/L as Mn	0.04	0.02	0.02	0.02	0	0	0	0	<0.018* 0**	-

Note:

* Base Case I = <0.018 g/L manganese
**Base Case II = 0.0 g/L manganese

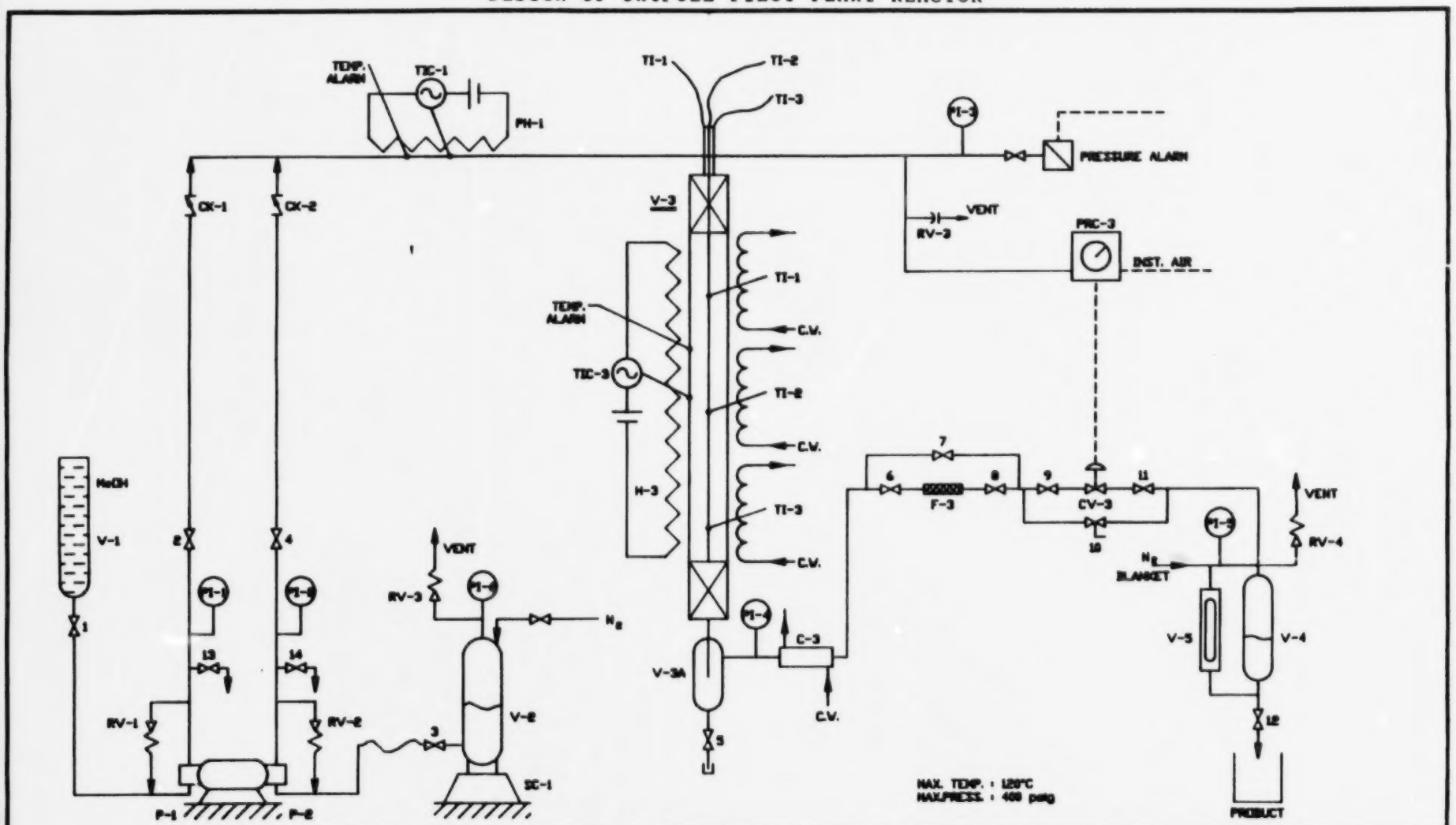
TABLE 54

REGULAR LEADED GASOLINE BLENDS
m^3/CD

	Base Case I				Base Case II				Specification	
	Base Case I	MTBE Plant	TAME Plant	MTBE + TAME Plant	Base Case II	MTBE Plant	TAME Plant	MTBE + TAME Plant	Max	Min
n-Butane	85.5	90	85.5	90	114	114	114	114	-	-
DiH Overheads	189	172	189	172	-	-	-	-	-	-
Reformate	464	476	464	476	572	617	572	572	-	-
Light Naphtha Gasoline	-	-	-	-	44.4	-	44.4	44.7	-	-
Isomerate	-	-	-	-	7.6	7.8	7.6	7.6	-	-
Reid Vapour Pressure	233	233	233	233	233	233	233	233	233	176
% Evaporated @ 82°C	50.0	50.0	50.0	50.0	39.7	39.8	39.7	39.7	50.0	-
% Evaporated @ 112°C	79.9	80.2	79.9	80.2	75.1	75.2	75.1	75.1	-	50.0
MON	87.2	87.2	87.2	87.2	86.7	86.6	86.7	86.7	-	83.0
Calc. Road O.N.	89.8	89.8	89.8	89.8	89.8	89.8	89.8	89.8	-	89.0
Lead g/L	0.10	0.29	0.10	0.29	0	0	0	0	<0.029* 0**	-

Note:

* Lead Specification = <0.29 g/L max for Base Case I
**Lead Specification = 0 for Base Base II



REV. NO.	DESCRIPTION	DATE	DRAWN BY	CHK'D BY	APP'D BY

DRAWN BY	B.P.
CHK'D BY	
APP'D BY	
PROJ. NO.	+ 98601

PETRO-CANADA LIMITED
RESEARCH AND DEVELOPMENT DEPARTMENT

OXYFUEL REACTOR UNIT

FLOWSHEET

PILOT PLANT

CLASS NO.	
DATE	11 MARCH/86
SCALE	NONE
DRAWING NO.	B-2354-RD-0

FIGURE 2

MTBE PROCESS INTEGRATED WITH REFINING COMPLEX

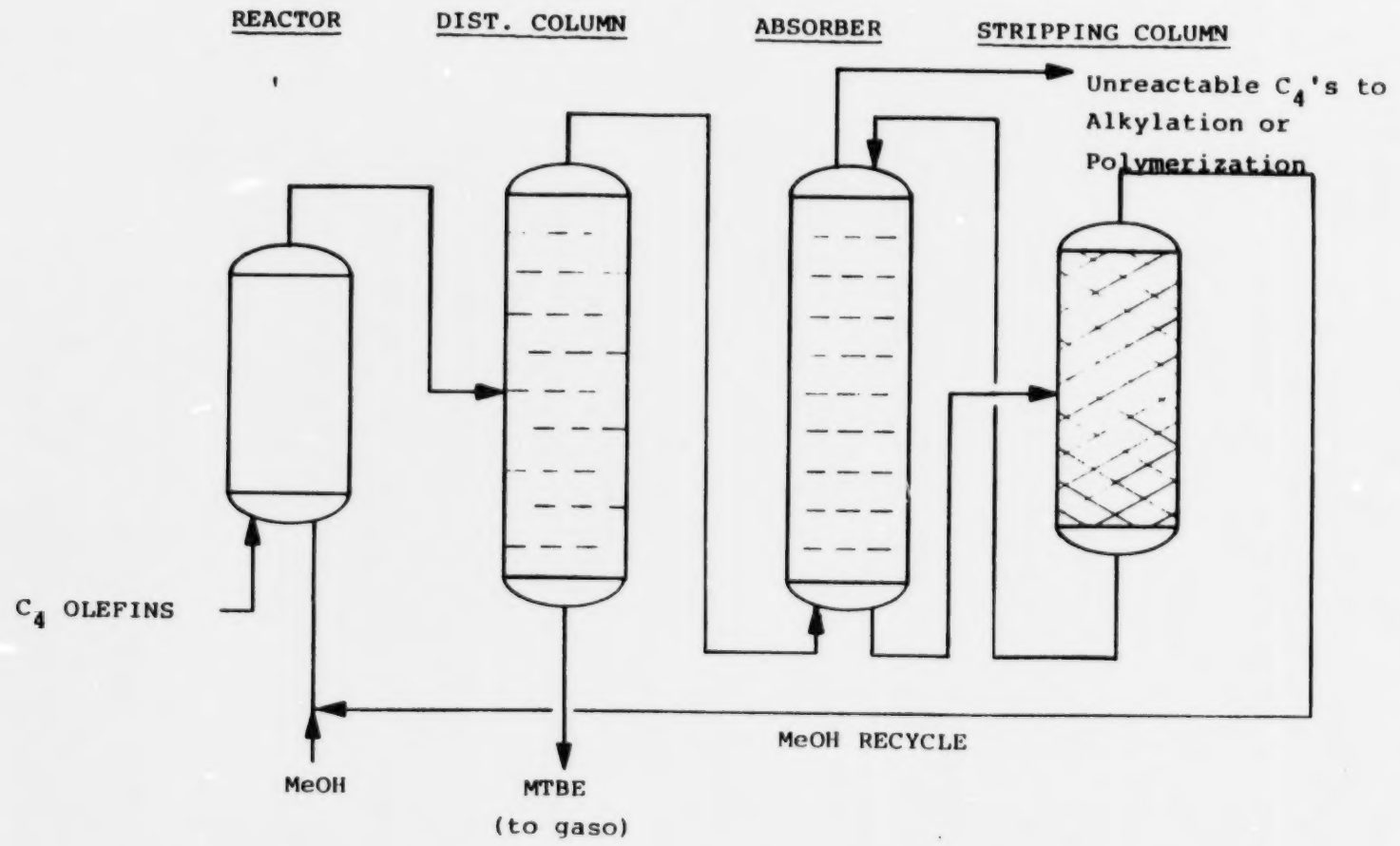


FIGURE 3

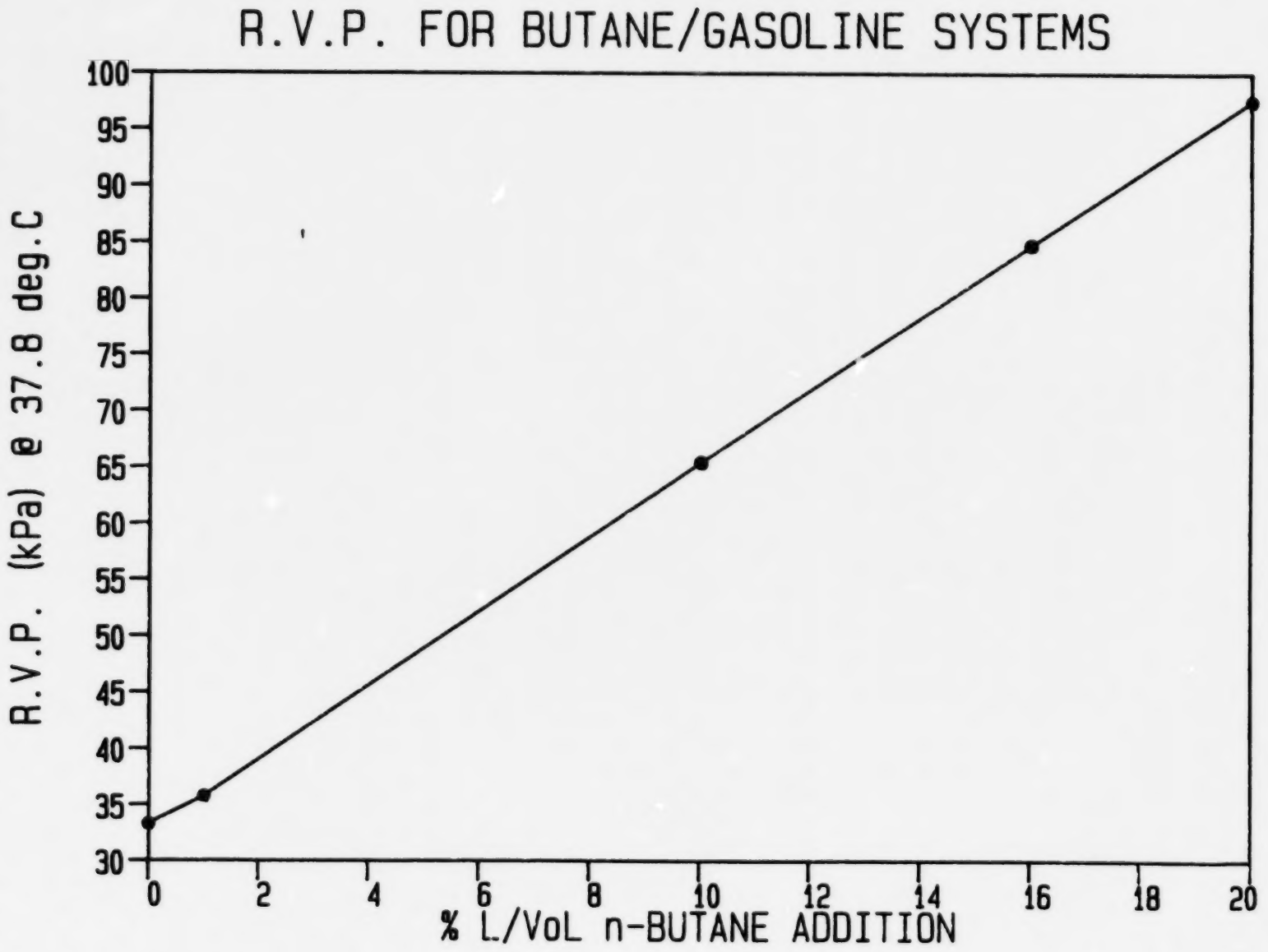

R.V.P. FOR BUTANE/GASOLINE SYSTEMS
R.V.P. (kPa) @ 37.8 deg.C
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
0
2
4
6
8
10
12
14
16
18
20
% L./VoL n-BUTANE ADDITION

FIGURE 4

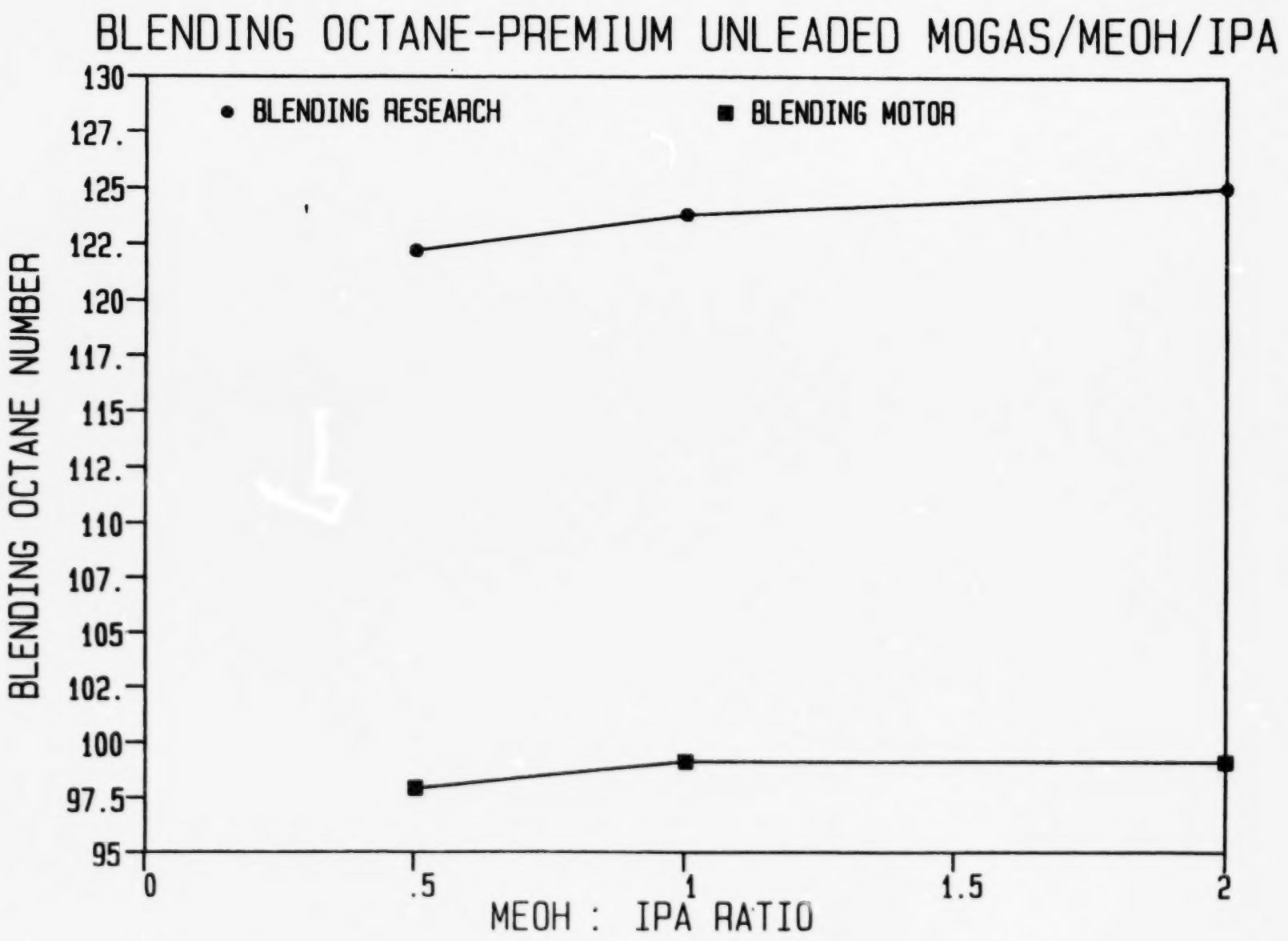

BLENDING OCTANE-PREMIUM UNLEADED MOGAS/MEOH/IPA
BLENDING RESEARCH
BLENDING MOTOR
BLENDING OCTANE NUMBER
130
127.
125
122.
120
117.
115
112.
110
107.
105
102.
100
97.5
95
0
.5
1
1.5
2
MEOH : IPA RATIO

FIGURE 5

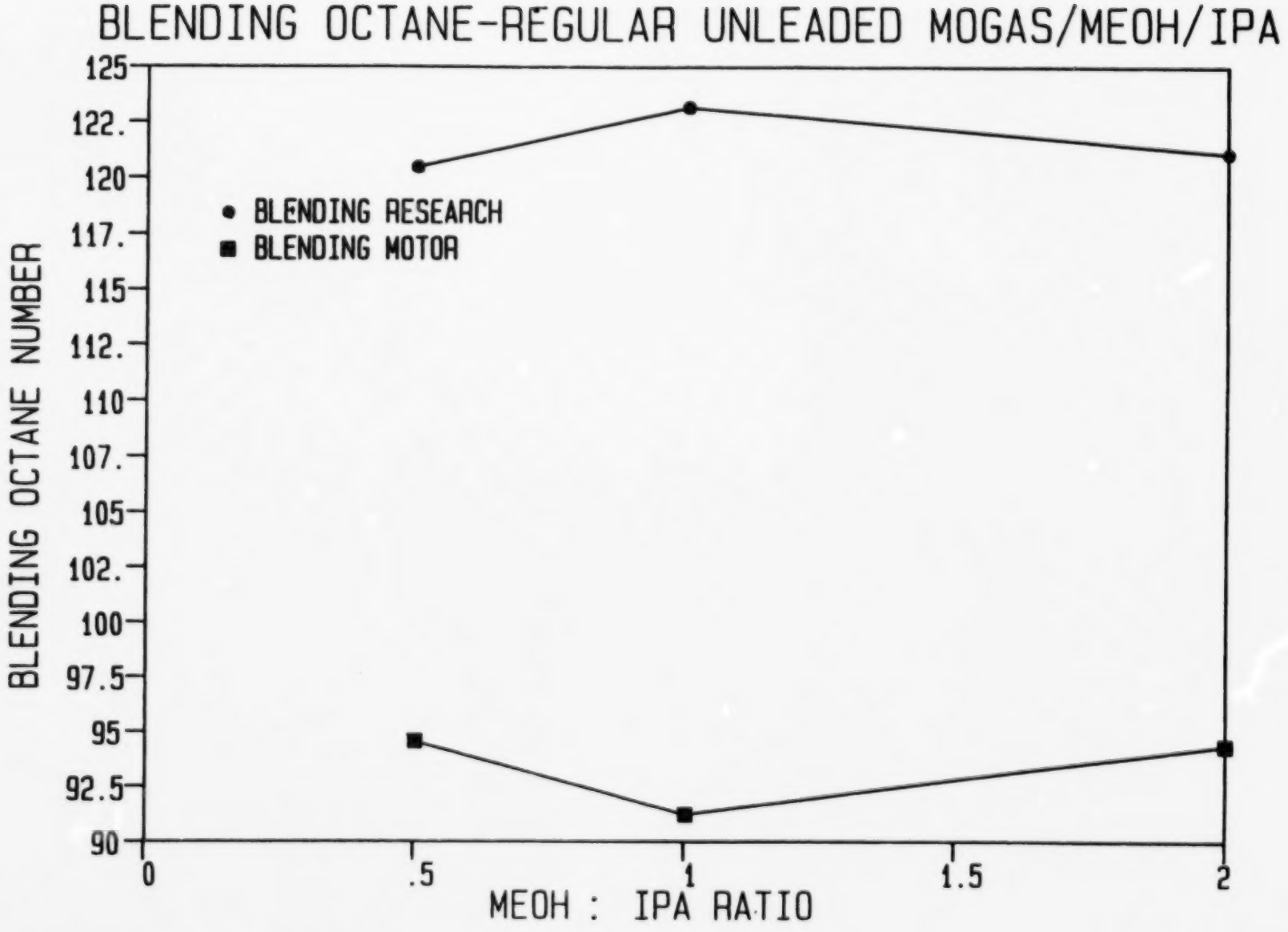

BLENDING OCTANE-REGULAR UNLEADED MOGAS/MEOH/IPA
BLENDING OCTANE NUMBER
125
122.
120
117.
115
112.
110
107.
105
102.
100
97.5
95
92.5
90
BLENDING RESEARCH
BLENDING MOTOR
0
.5
1
1.5
2
MEOH : IPA RATIO

FIGURE 6

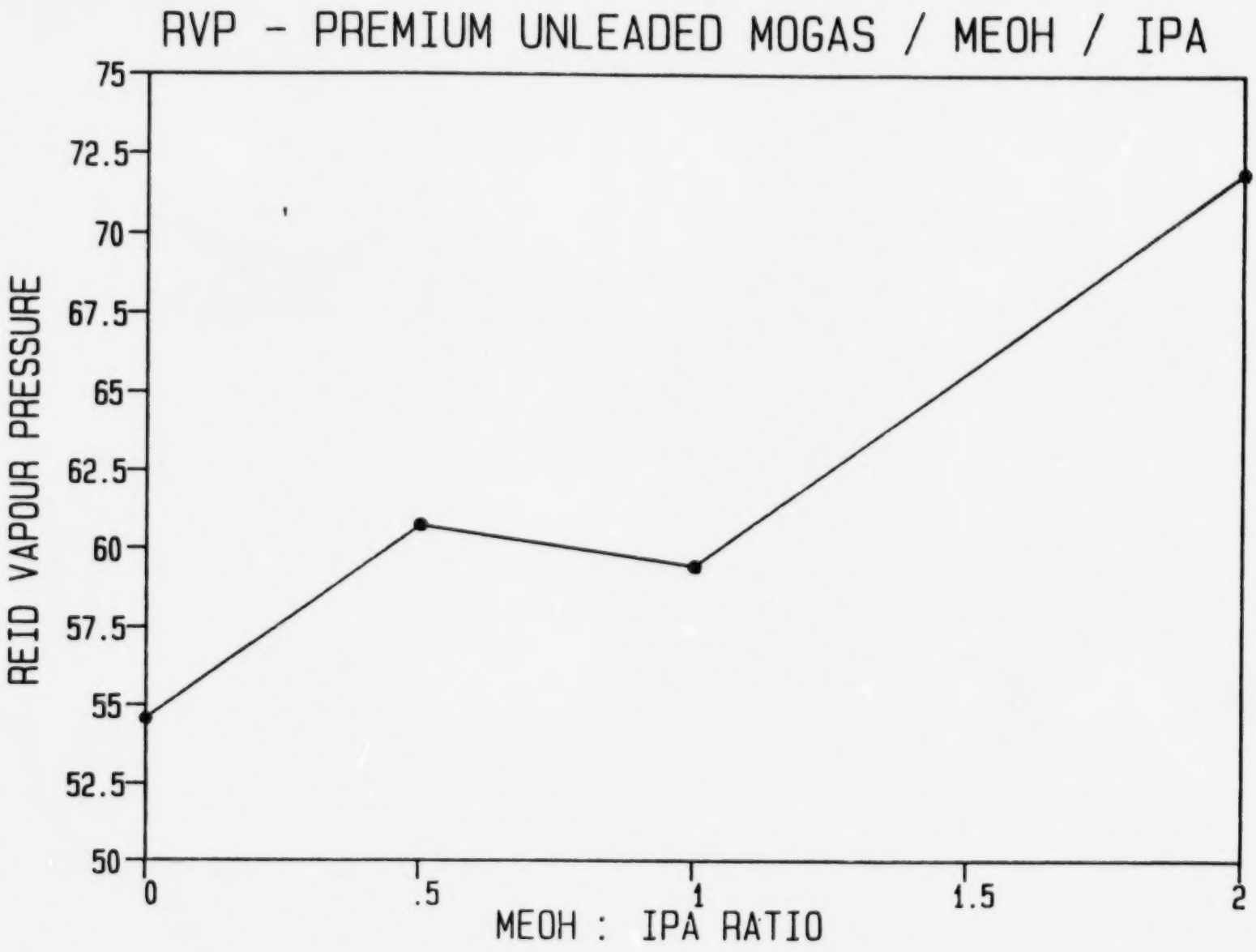

RVP - PREMIUM UNLEADED MOGAS / MEOH / IPA
REID VAPOUR PRESSURE
75
72.5
70
67.5
65
62.5
60
57.5
55
52.5
50
0
.5
1
1.5
2
MEOH : IPA RATIO

FIGURE 7

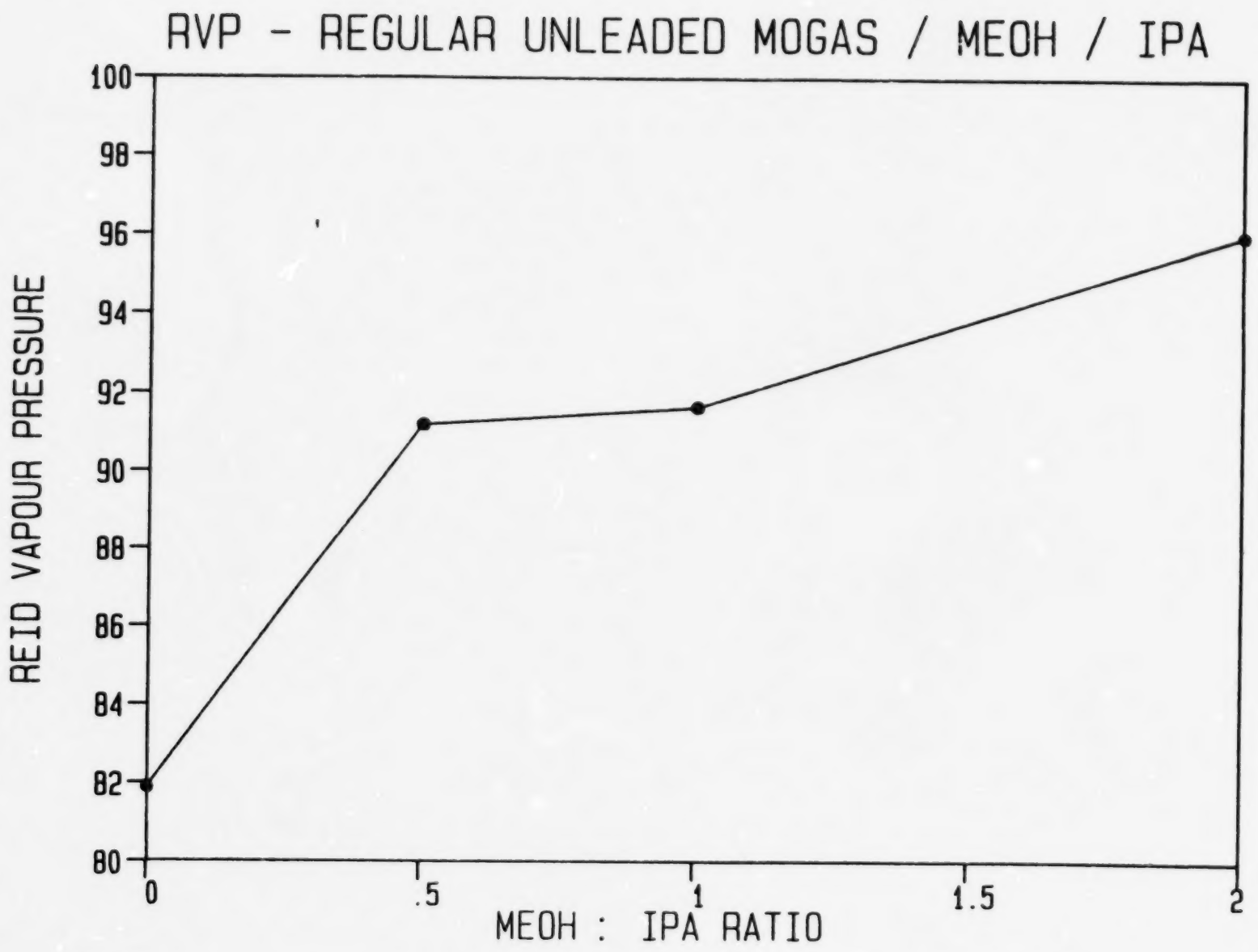

RVP - REGULAR UNLEADED MOGAS / MEOH / IPA
REID VAPOUR PRESSURE
100
98
96
94
92
90
88
86
84
82
80
0
.5
1
1.5
2
MEOH : IPA RATIO

FIGURE 8

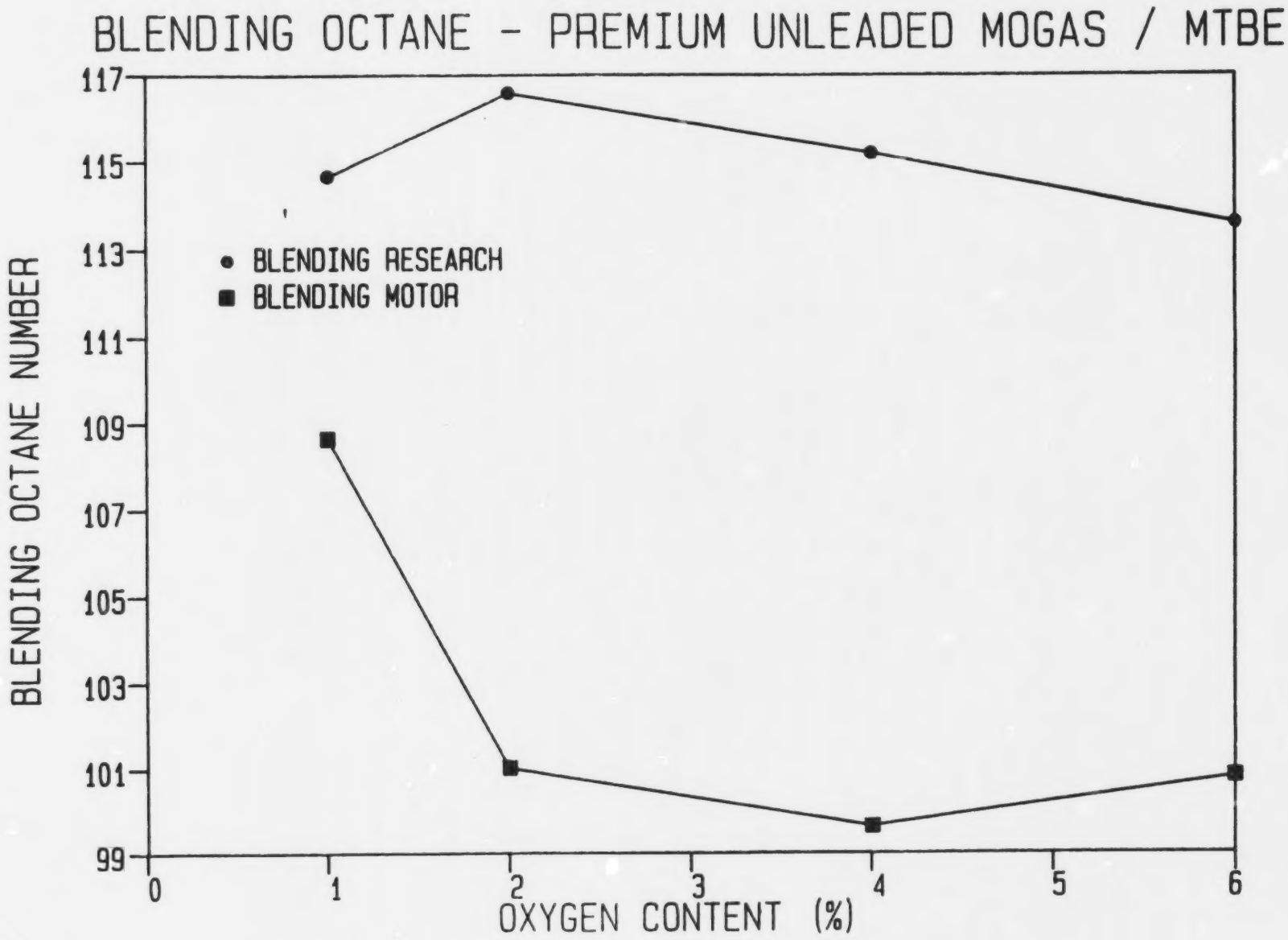

BLENDING OCTANE - PREMIUM UNLEADED MOGAS / MTBE
BLENDING OCTANE NUMBER
117
115
113
111
109
107
105
103
101
99
BLENDING RESEARCH
BLENDING MOTOR
0
1
2
3
4
5
6
OXYGEN CONTENT (%)

FIGURE 9

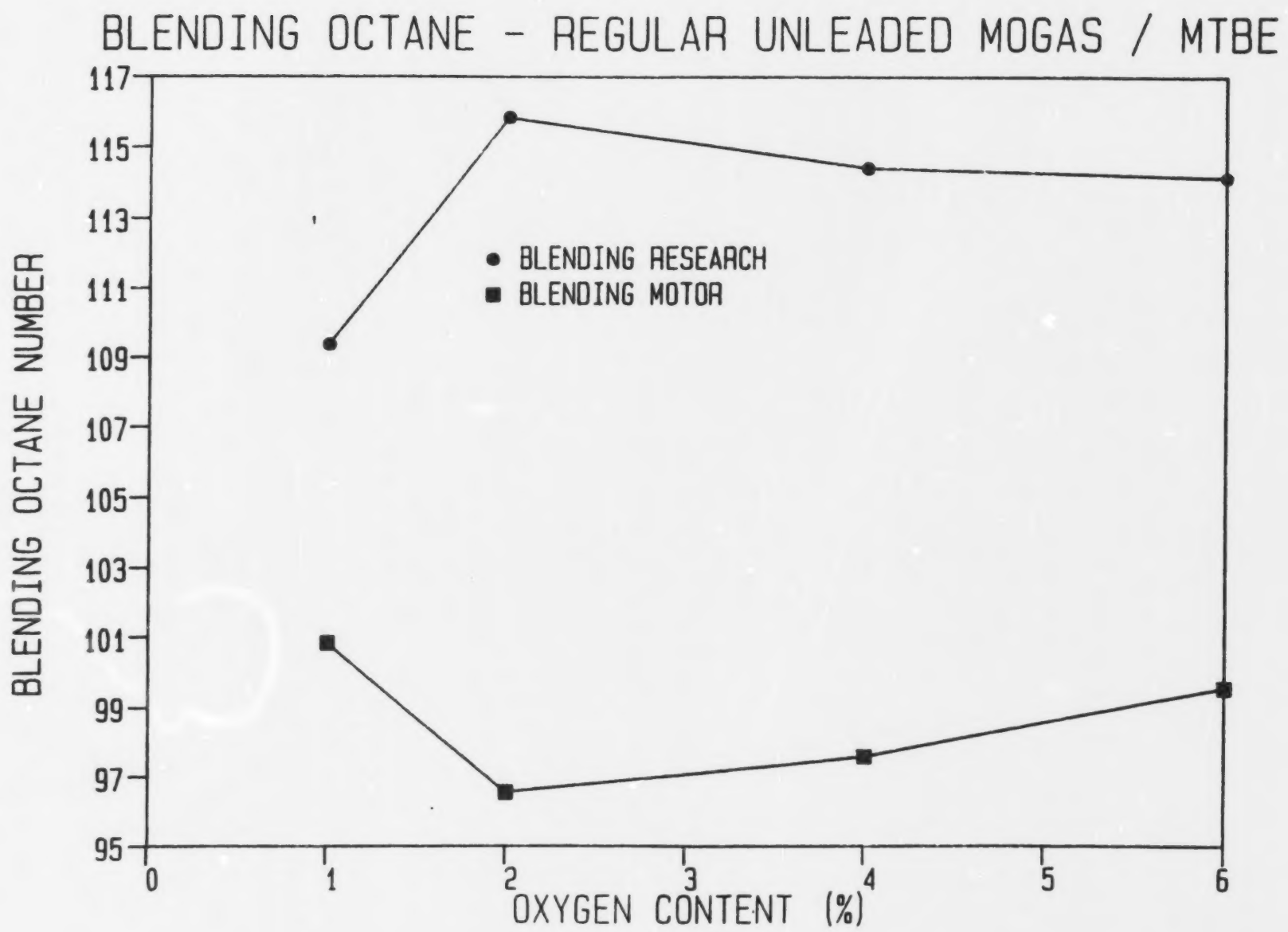

BLENDING OCTANE - REGULAR UNLEADED MOGAS / MTBE
BLENDING OCTANE NUMBER
117
115
113
111
109
107
105
103
101
99
97
95
BLENDING RESEARCH
BLENDING MOTOR
0
1
2
3
4
5
6
OXYGEN CONTENT (%)

FIGURE 10

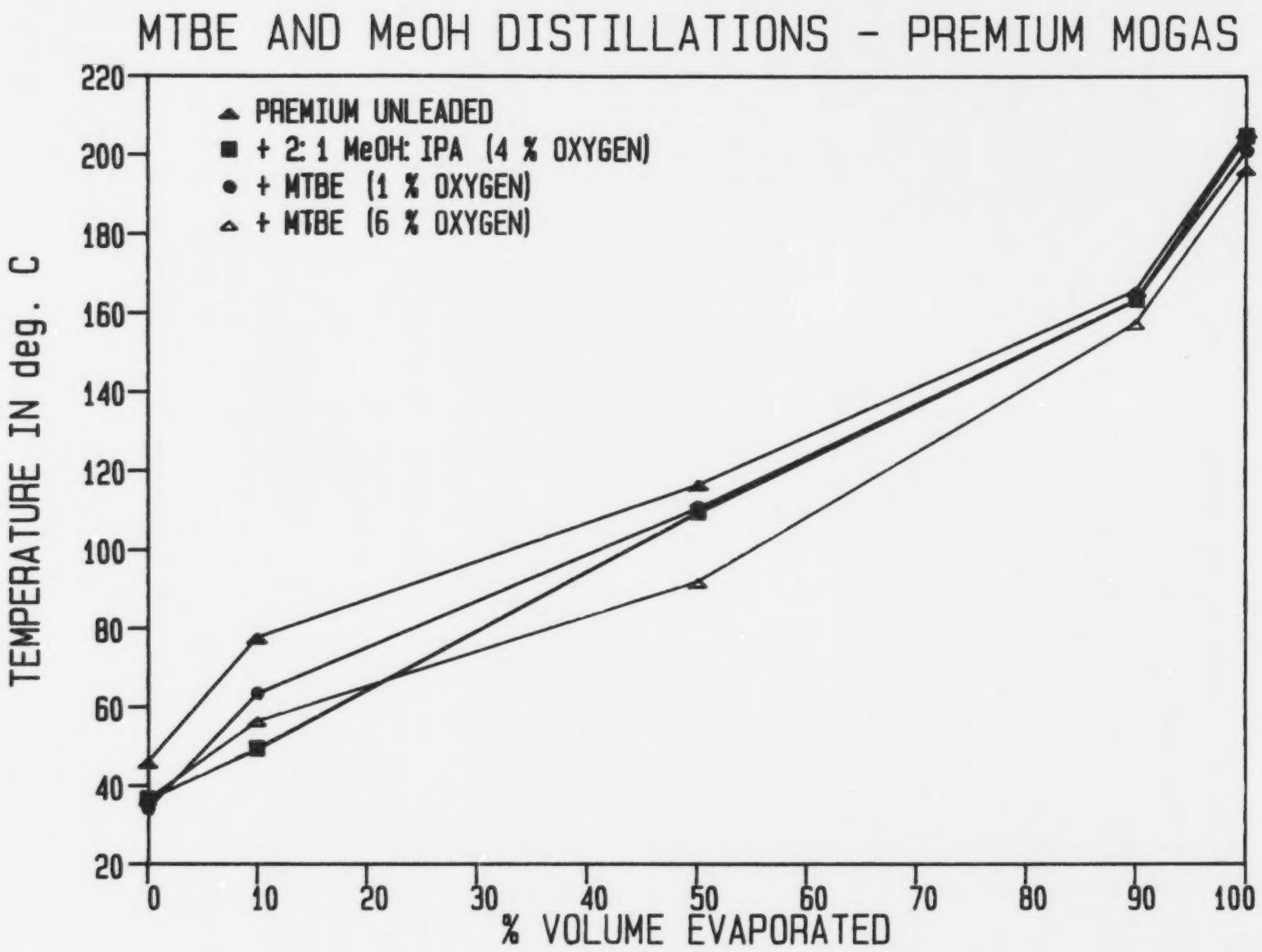

MTBE AND MeOH DISTILLATIONS - PREMIUM MOGAS
PREMIUM UNLEADED
+ 2:1 MeOH:IPA (4 % OXYGEN)
+ MTBE (1 % OXYGEN)
+ MTBE (6 % OXYGEN)
TEMPERATURE IN deg. C
220
200
180
160
140
120
100
80
60
40
20
0
10
20
30
40
50
60
70
80
90
100
% VOLUME EVAPORATED

FIGURE 11

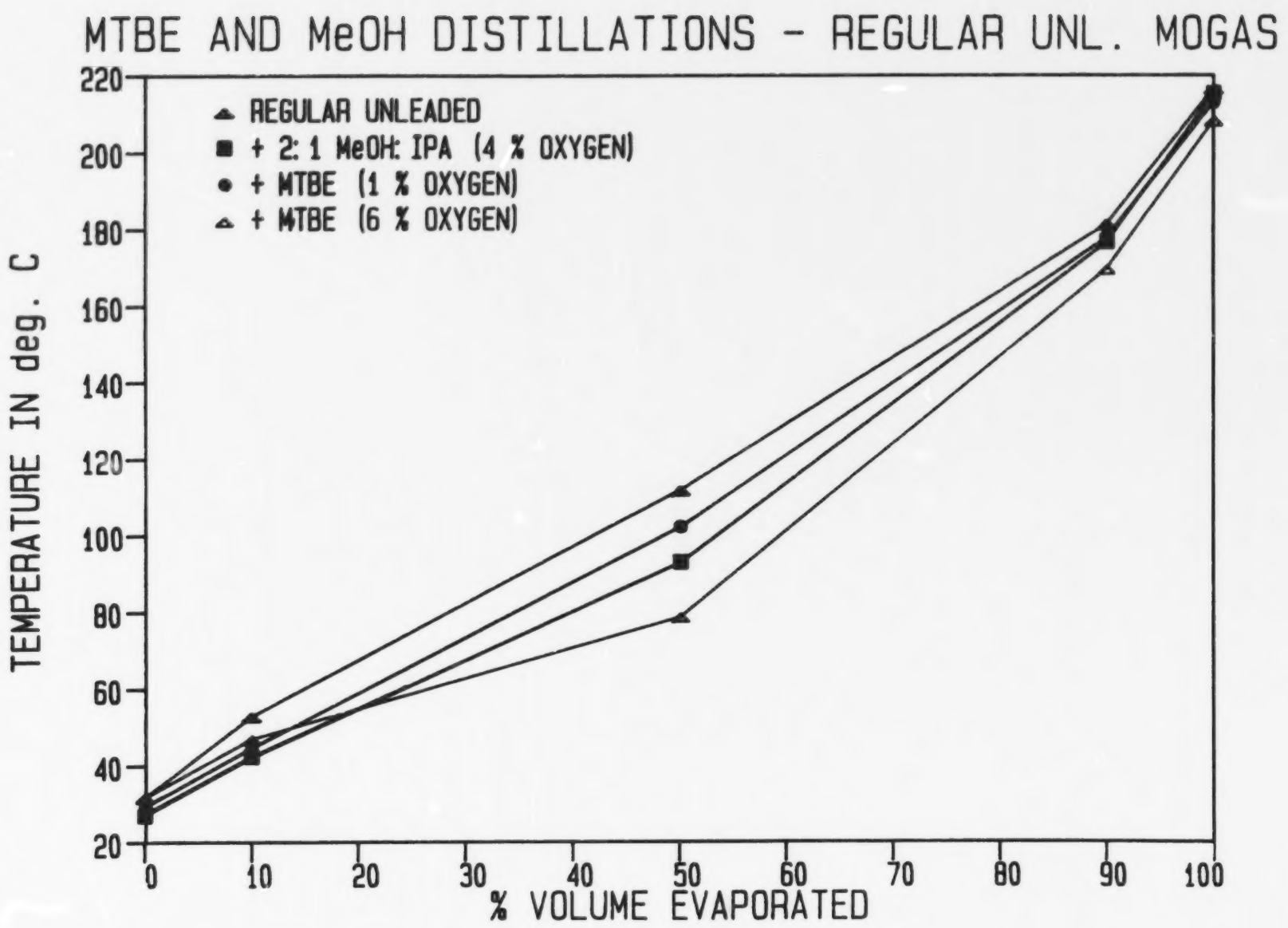

MTBE AND MeOH DISTILLATIONS - REGULAR UNL. MOGAS
REGULAR UNLEADED
+ 2:1 MeOH: IPA (4 % OXYGEN)
+ MTBE (1 % OXYGEN)
+ MTBE (6 % OXYGEN)
TEMPERATURE IN deg. C
220
200
180
160
140
120
100
80
60
40
20
0
10
20
30
40
50
60
70
80
90
100
% VOLUME EVAPORATED

FIGURE 12

TAME Process Integrated with Refining Complex

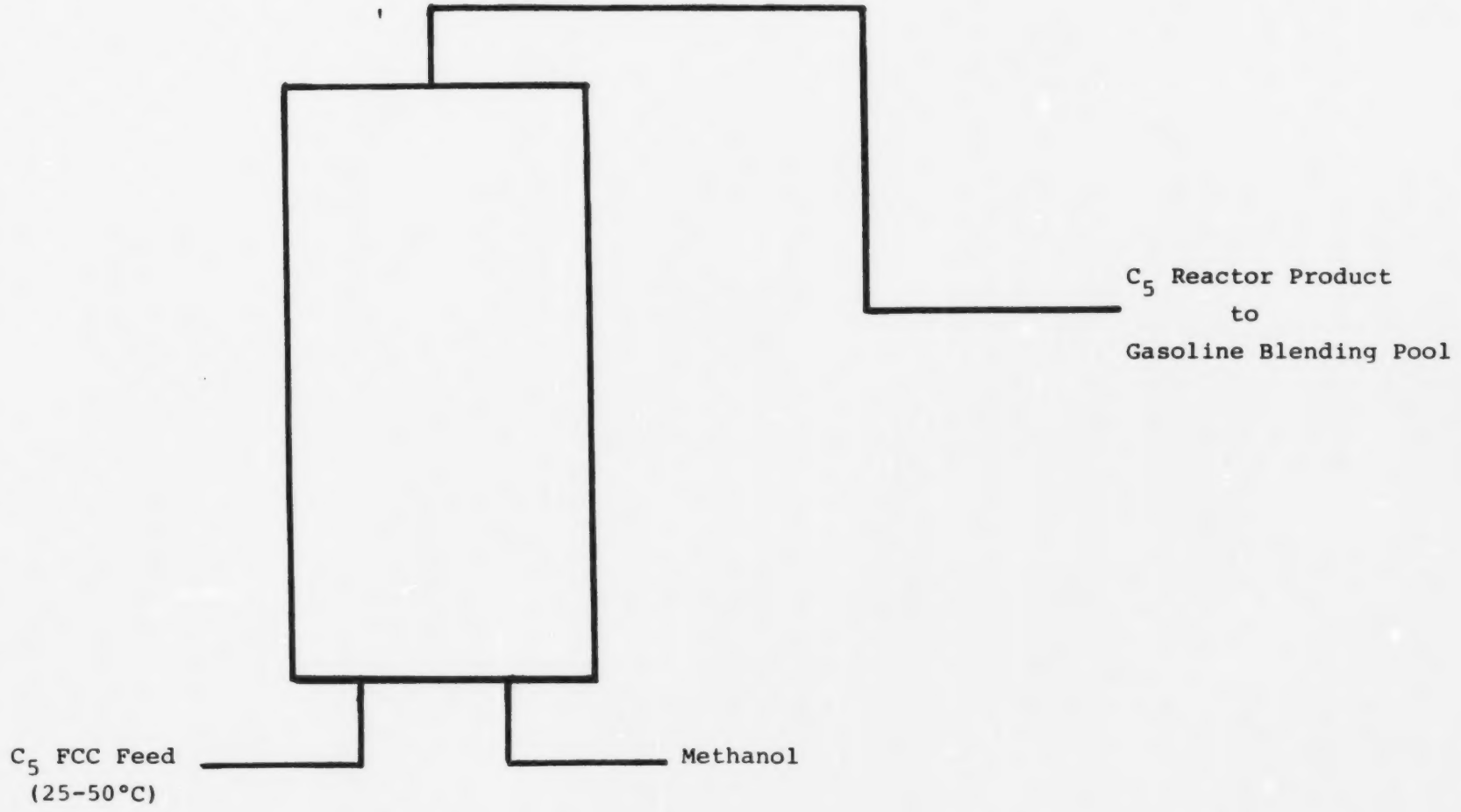


FIGURE 13

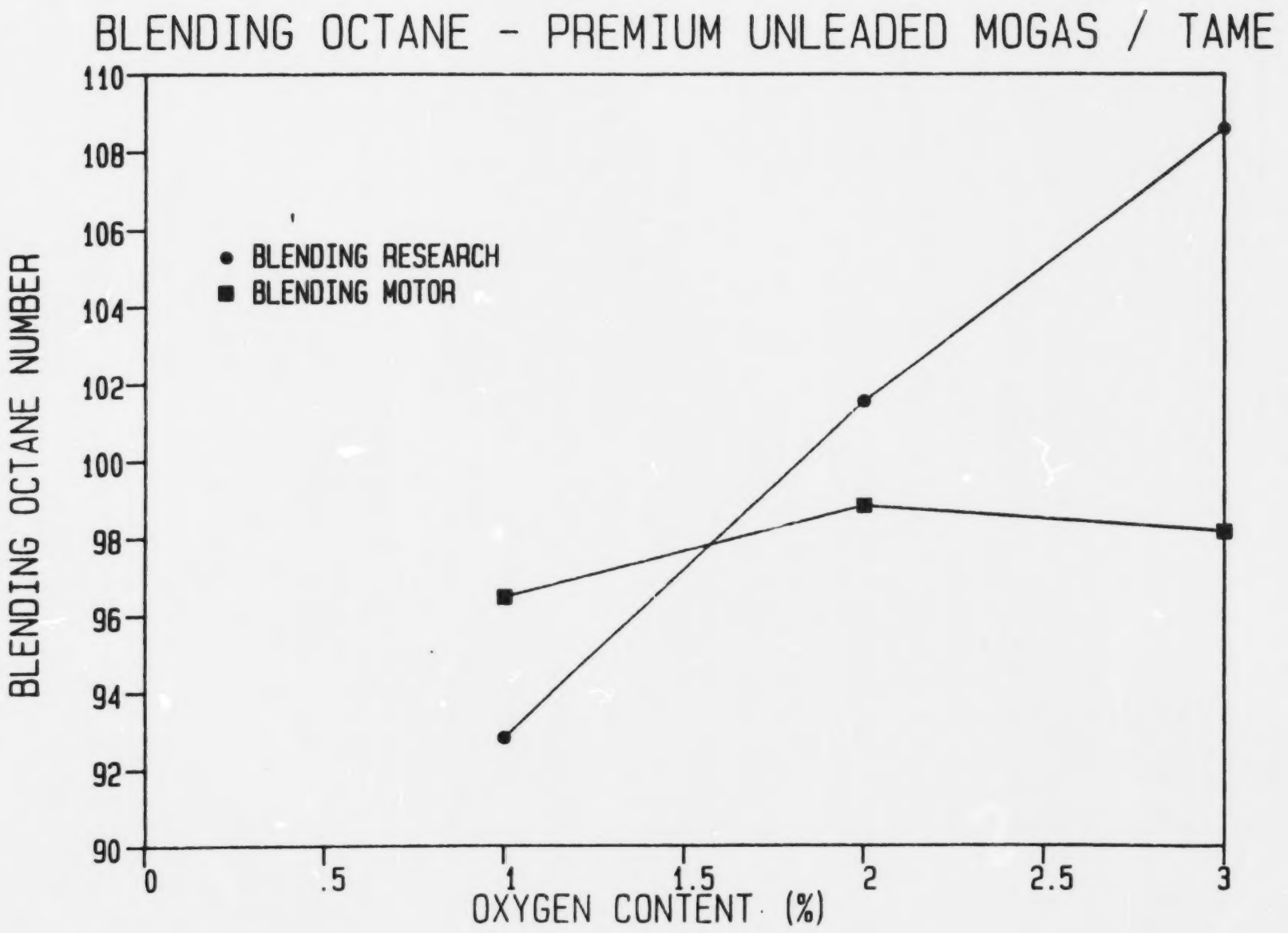

BLENDING OCTANE - PREMIUM UNLEADED MOGAS / TAME
BLENDING OCTANE NUMBER
110
108
106
104
102
100
98
96
94
92
90
BLENDING RESEARCH
BLENDING MOTOR
0
.5
1
1.5
2
2.5
3
OXYGEN CONTENT (%)

FIGURE 14

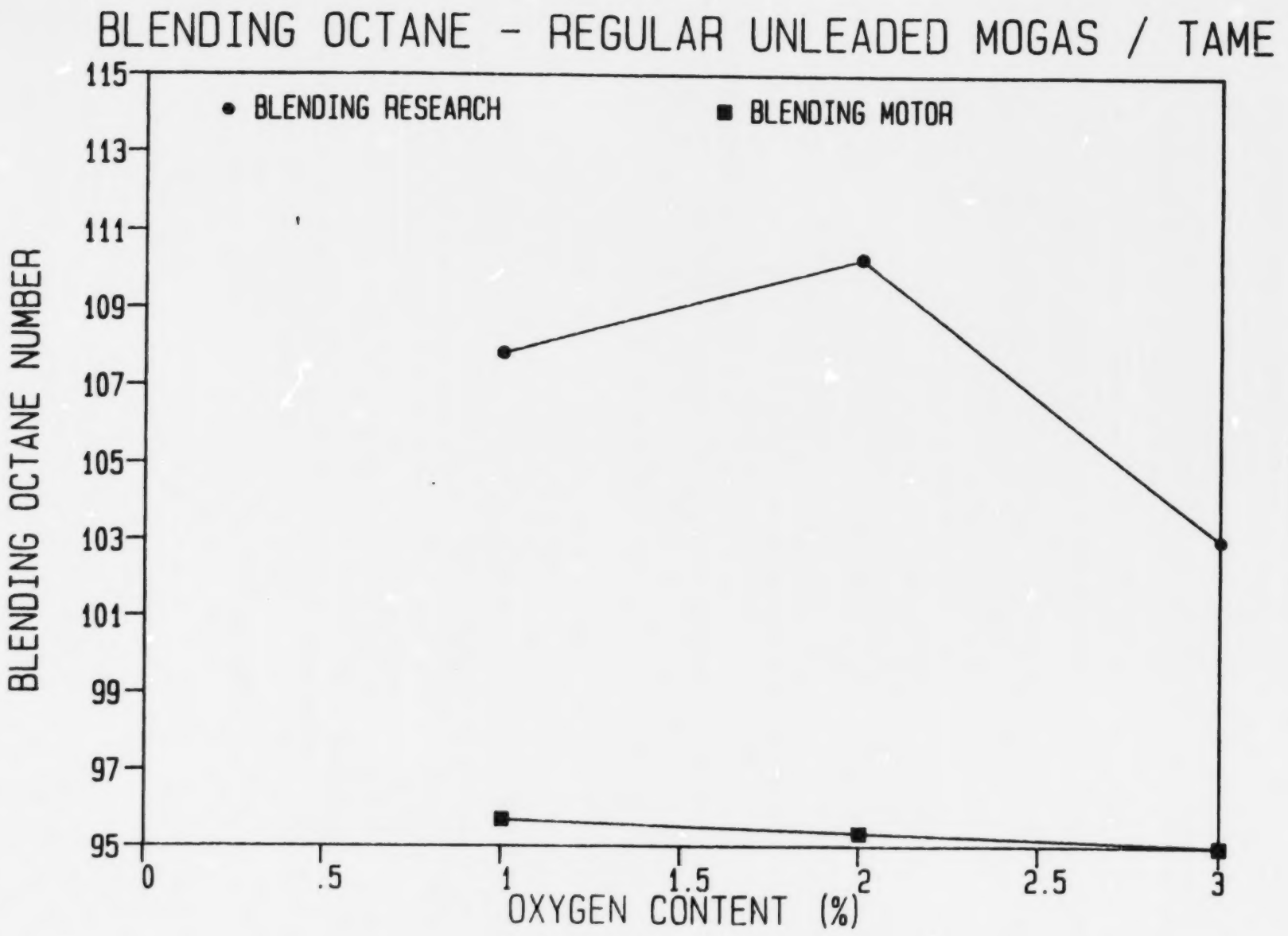

BLENDING OCTANE - REGULAR UNLEADED MOGAS / TAME
BLENDING RESEARCH
BLENDING MOTOR
BLENDING OCTANE NUMBER
115
113
111
109
107
105
103
101
99
97
95
0
.5
1
1.5
2
2.5
3
OXYGEN CONTENT (%)

FIGURE 15

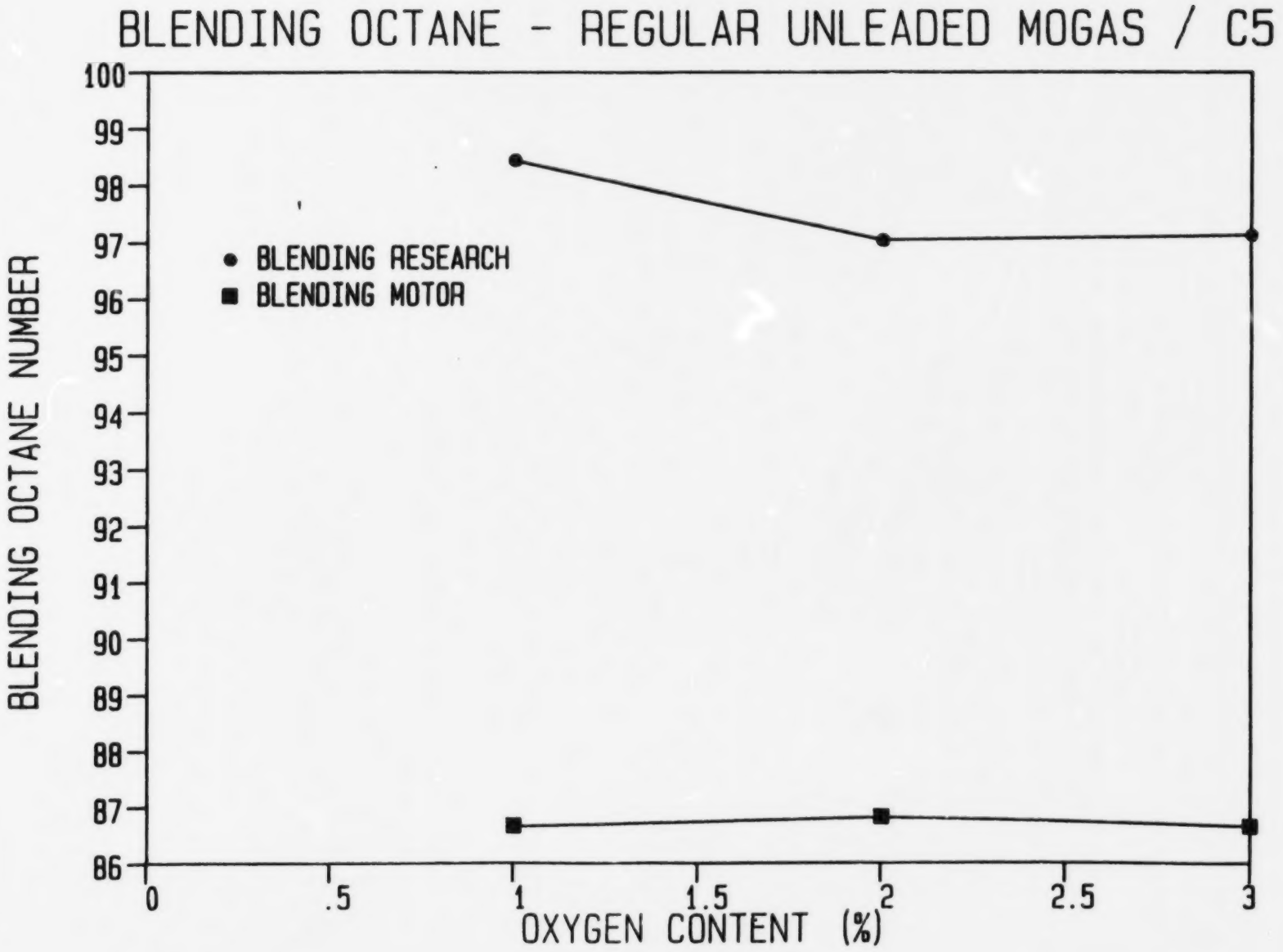

BLENDING OCTANE - REGULAR UNLEADED MOGAS / C5
BLENDING OCTANE NUMBER
100
99
98
97
96
95
94
93
92
91
90
89
88
87
86
BLENDING RESEARCH
BLENDING MOTOR
0
.5
1
1.5
2
2.5
3
OXYGEN CONTENT (%)

FIGURE 16

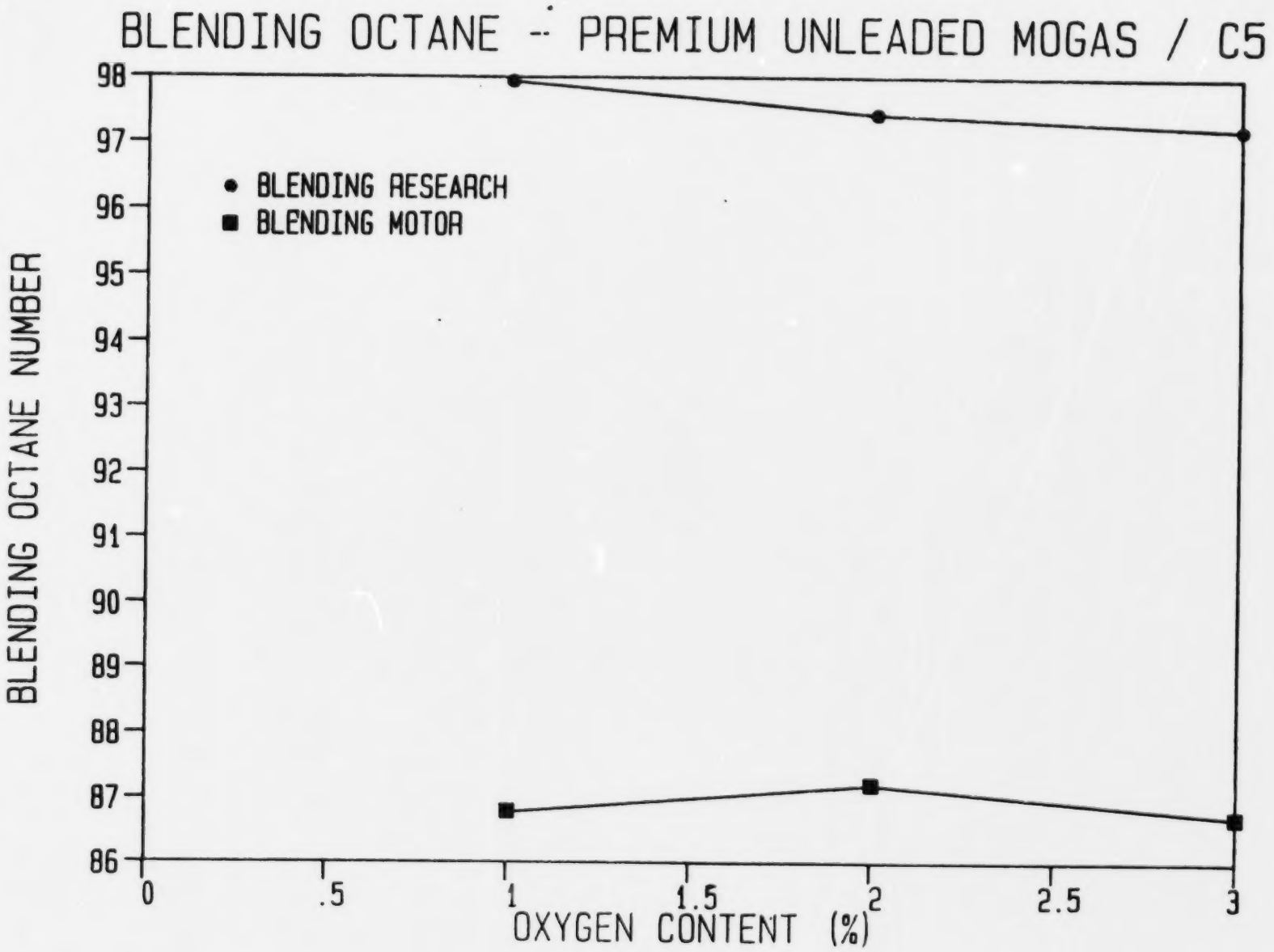

BLENDING OCTANE -- PREMIUM UNLEADED MOGAS / C5
BLENDING OCTANE NUMBER
98
97
96
95
94
93
92
91
90
89
88
87
86
BLENDING RESEARCH
BLENDING MOTOR
0
.5
1
1.5
2
2.5
3
OXYGEN CONTENT (%)

FIGURE 17

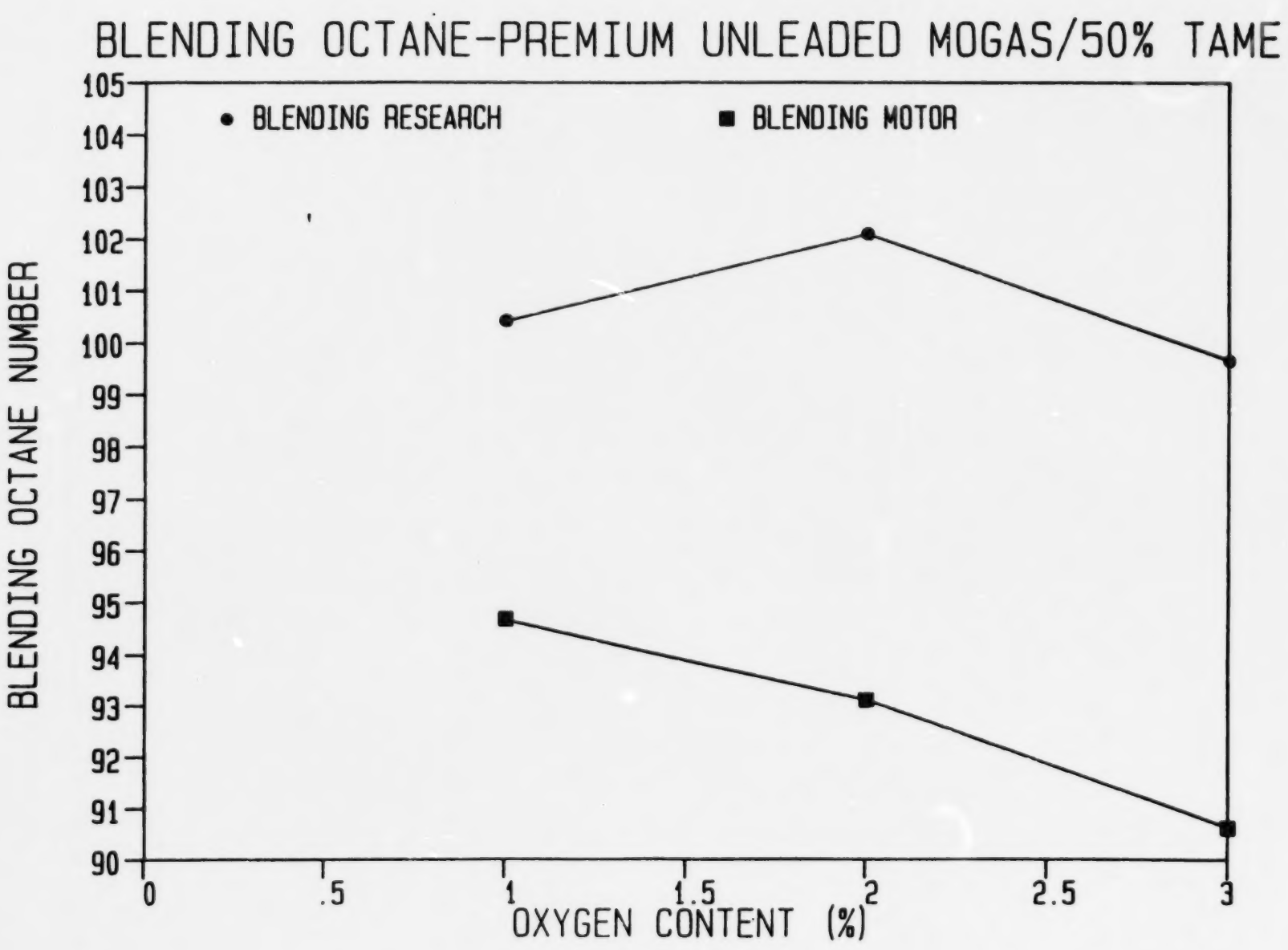

BLENDING OCTANE-PREMIUM UNLEADED MOGAS/50% TAME
BLENDING RESEARCH
BLENDING MOTOR
BLENDING OCTANE NUMBER
105
104
103
102
101
100
99
98
97
96
95
94
93
92
91
90
0
.5
1
1.5
2
2.5
3
OXYGEN CONTENT (%)

FIGURE 18

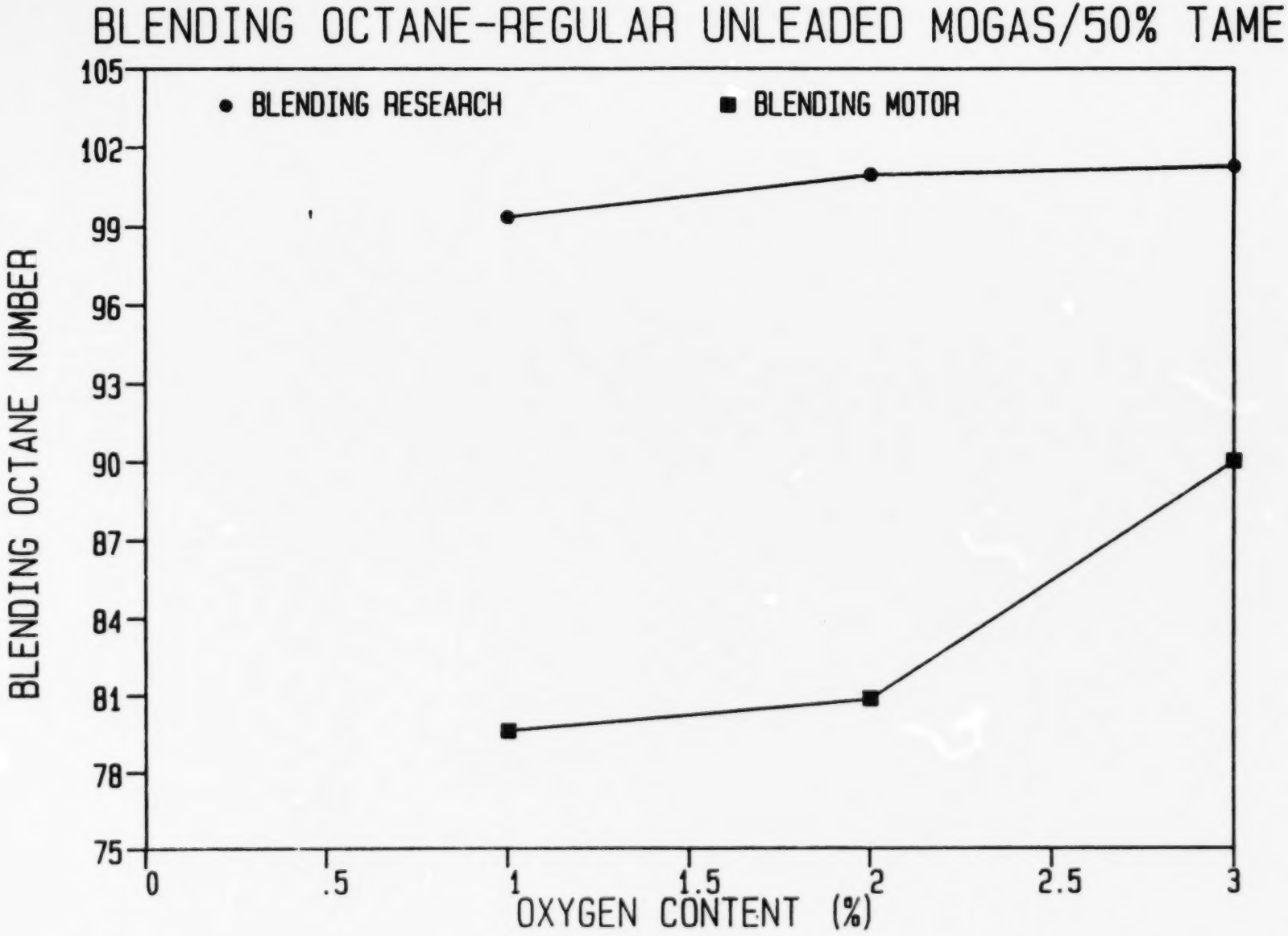

BLENDING OCTANE-REGULAR UNLEADED MOGAS/50% TAME
BLENDING RESEARCH
BLENDING MOTOR
BLENDING OCTANE NUMBER
105
102
99
96
93
90
87
84
81
78
75
0
.5
1
1.5
2
2.5
3
OXYGEN CONTENT (%)

FIGURE 19

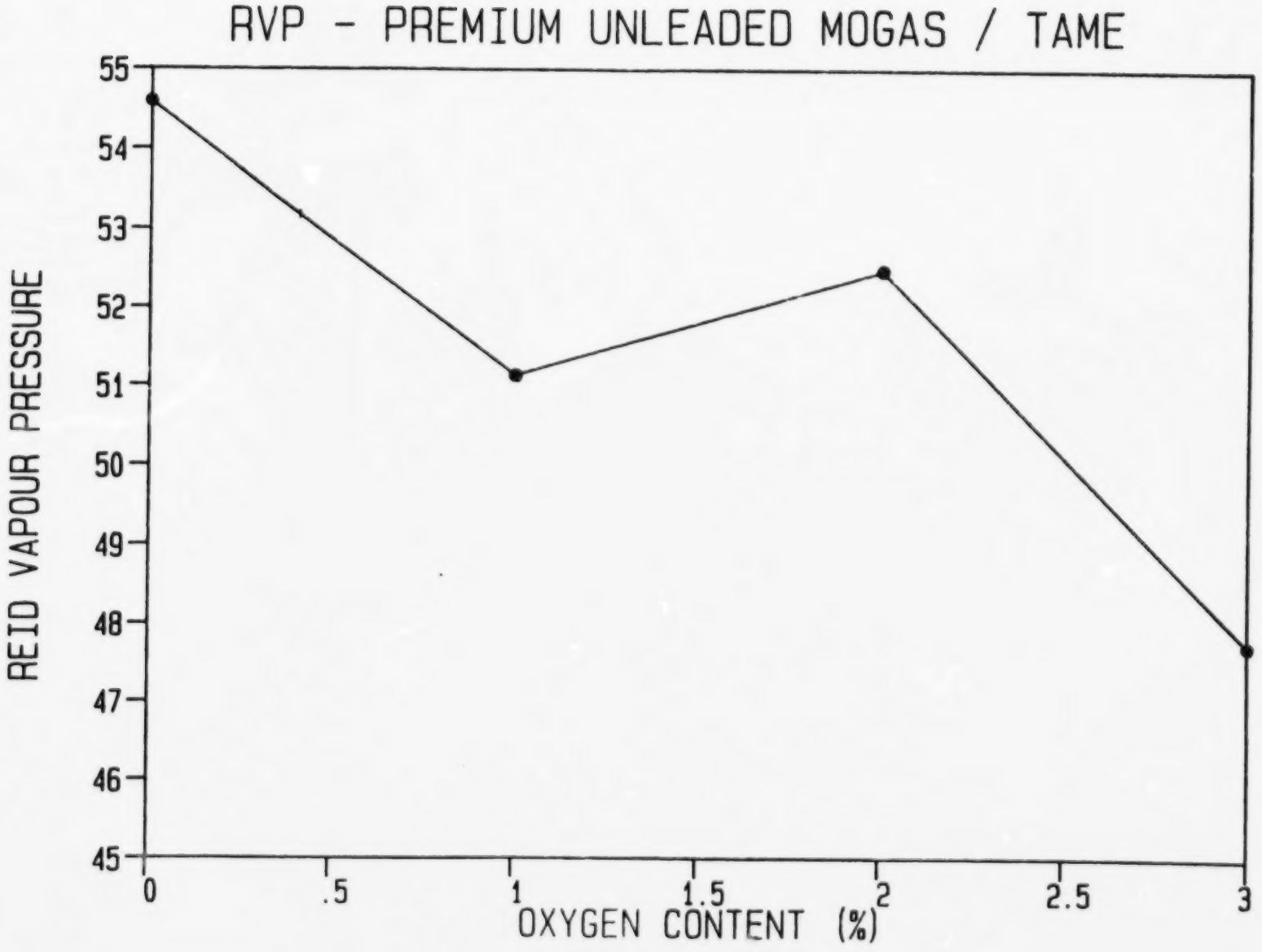

RVP - PREMIUM UNLEADED MOGAS / TAME
REID VAPOUR PRESSURE
55
54
53
52
51
50
49
48
47
46
45
0
.5
1
1.5
2
2.5
3
OXYGEN CONTENT (%)

FIGURE 20

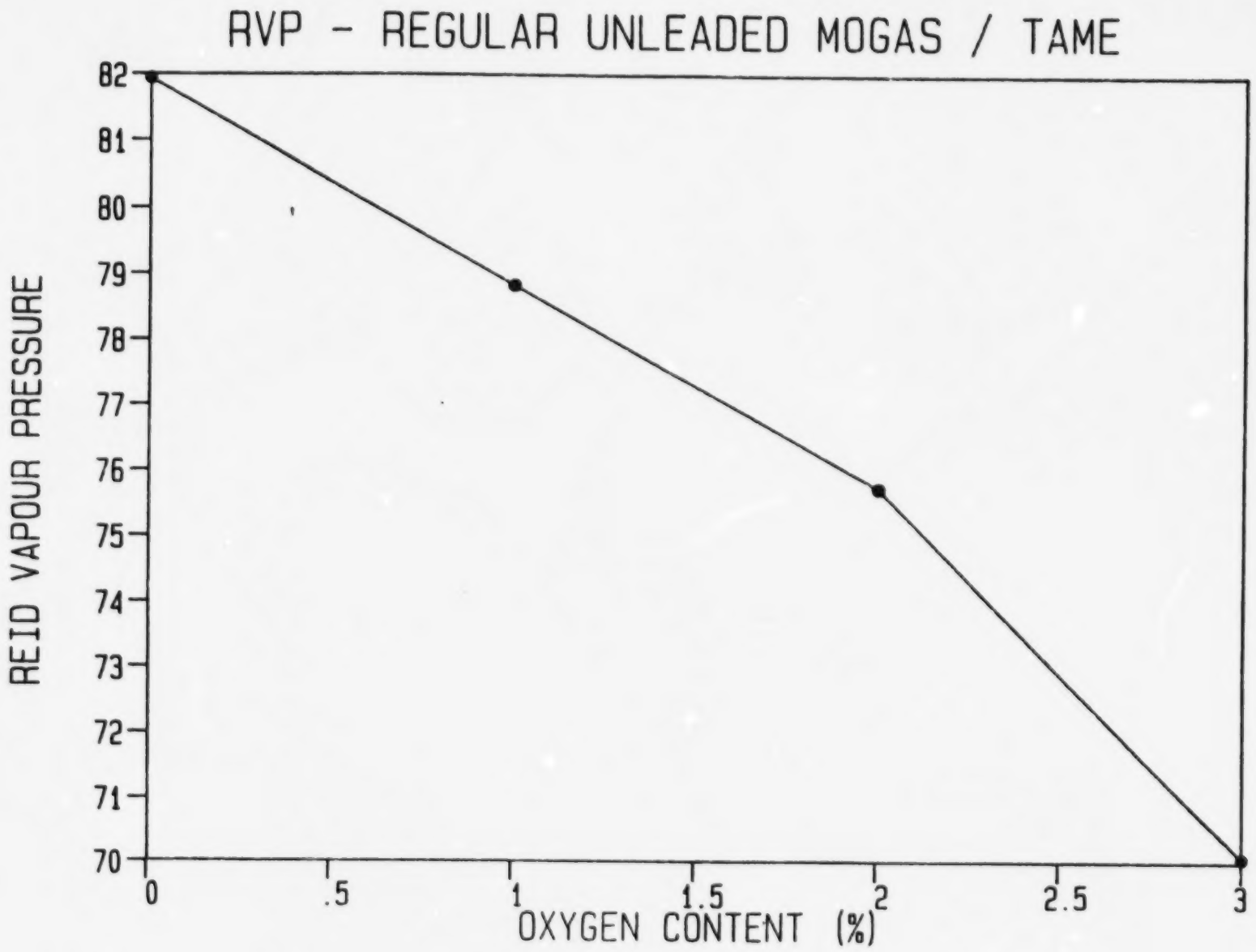

RVP - REGULAR UNLEADED MOGAS / TAME
REID VAPOUR PRESSURE
82
81
80
79
78
77
76
75
74
73
72
71
70
0
.5
1
1.5
2
2.5
3
OXYGEN CONTENT (%)

FIGURE 21

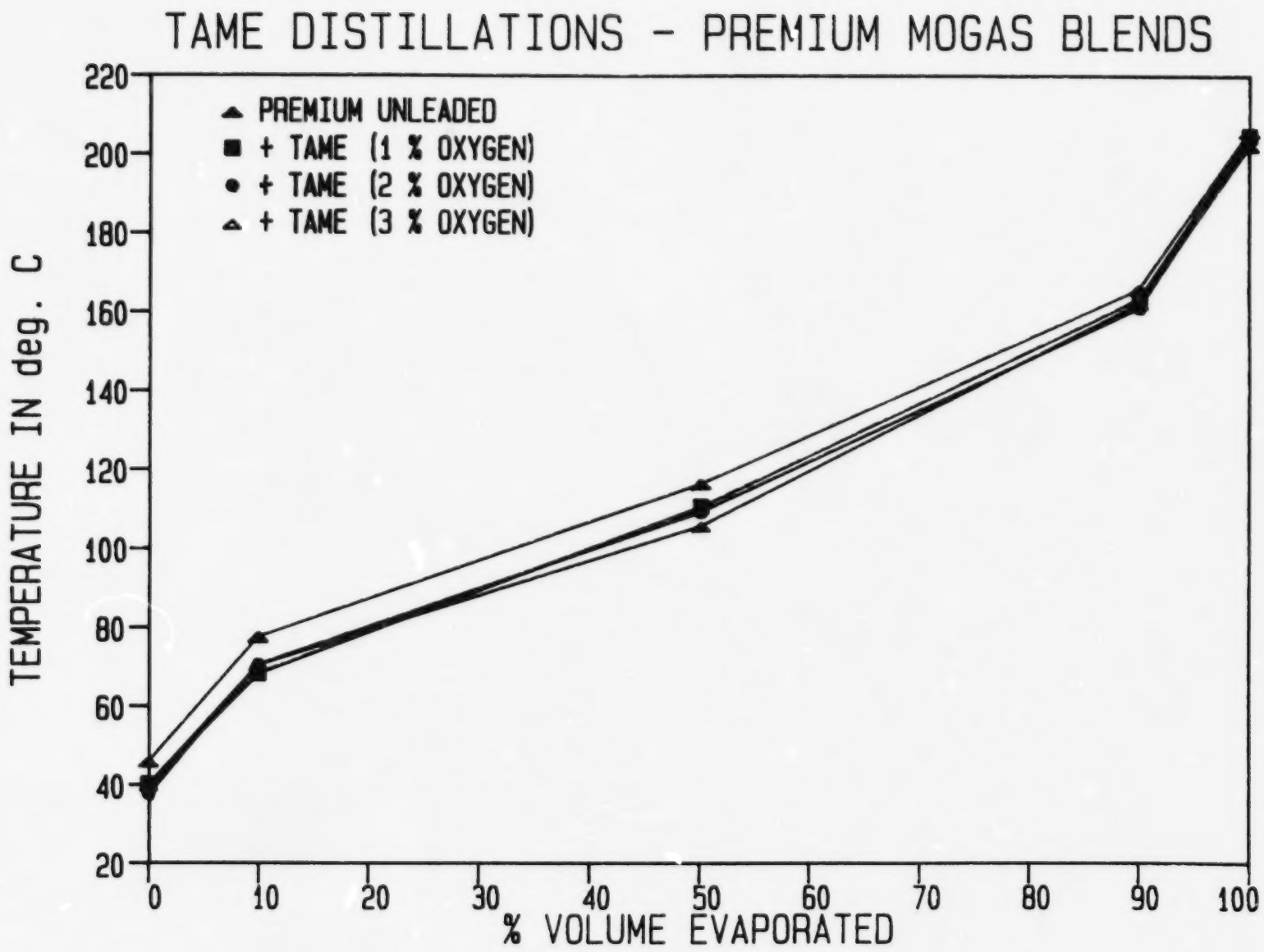

TAME DISTILLATIONS - PREMIUM MOGAS BLENDS
PREMIUM UNLEADED
+ TAME (1 % OXYGEN)
+ TAME (2 % OXYGEN)
+ TAME (3 % OXYGEN)
TEMPERATURE IN deg. C
220
200
180
160
140
120
100
80
60
40
20
0
10
20
30
40
50
60
70
80
90
100
% VOLUME EVAPORATED

FIGURE 22

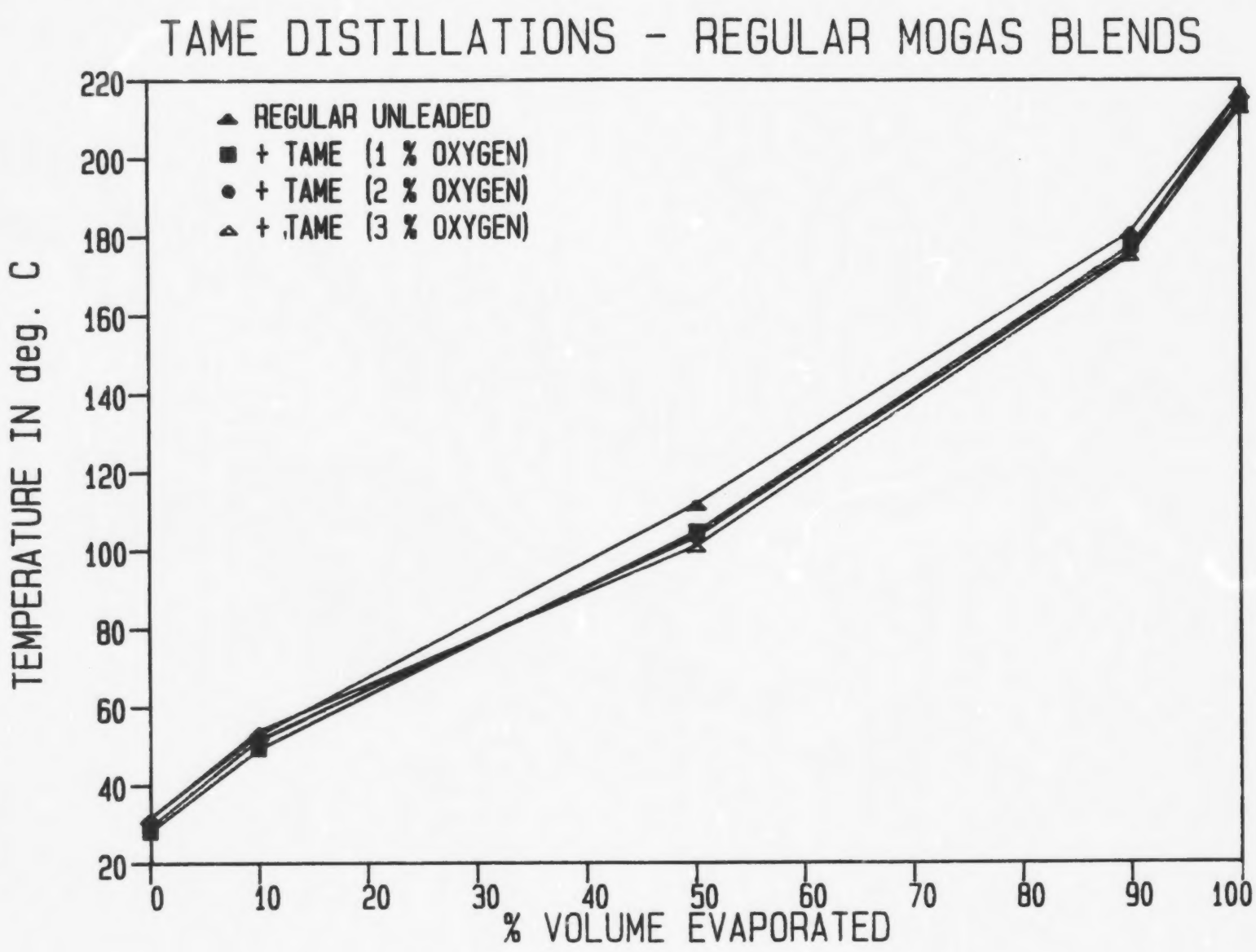

TAME DISTILLATIONS - REGULAR MOGAS BLENDS
REGULAR UNLEADED
+ TAME (1 % OXYGEN)
+ TAME (2 % OXYGEN)
+ TAME (3 % OXYGEN)
TEMPERATURE IN deg. C
220
200
180
160
140
120
100
80
60
40
20
0
10
20
30
40
50
60
70
80
90
100
% VOLUME EVAPORATED

FIGURE 23

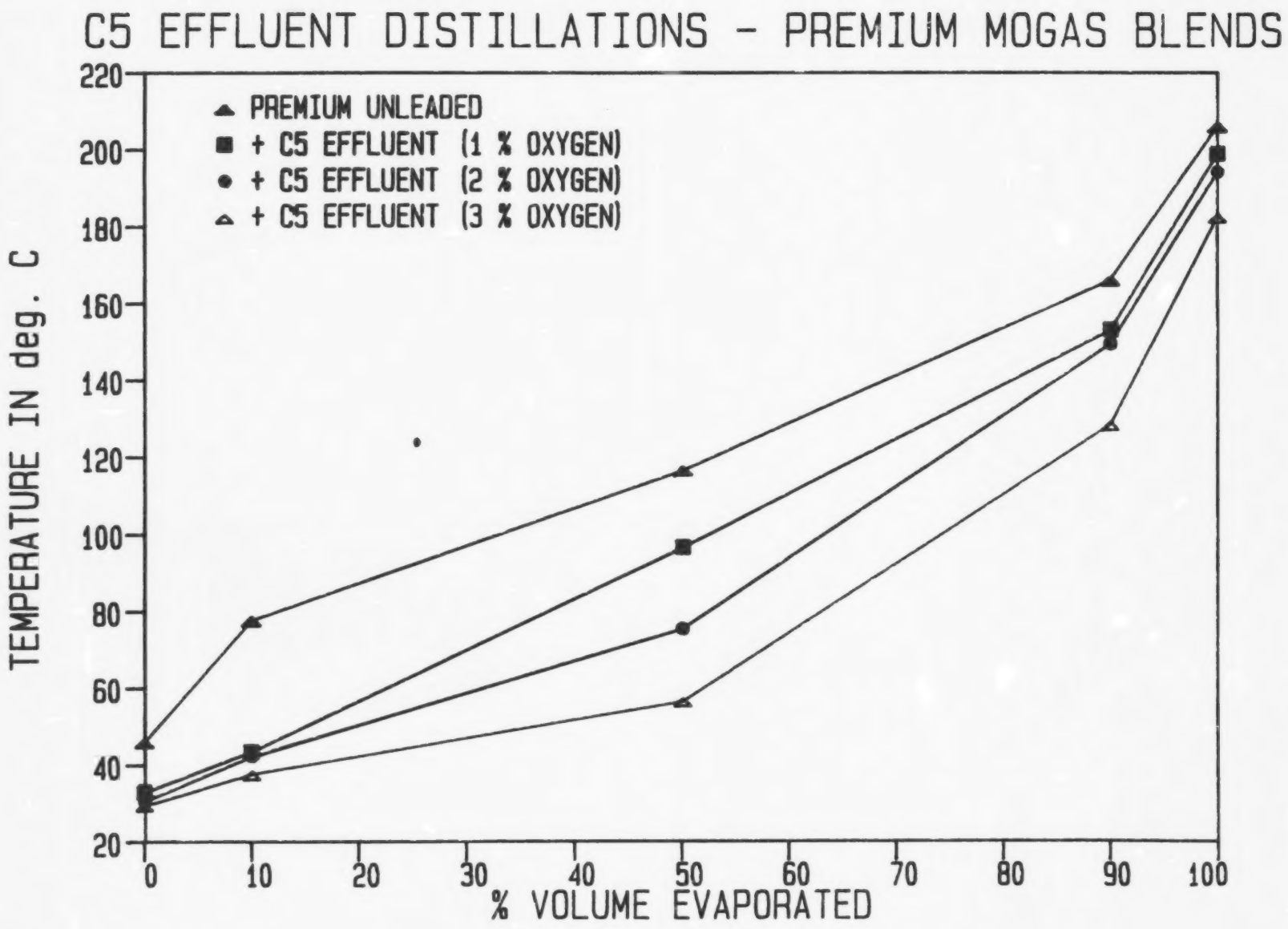

C5 EFFLUENT DISTILLATIONS - PREMIUM MOGAS BLENDS
PREMIUM UNLEADED
+ C5 EFFLUENT (1 % OXYGEN)
+ C5 EFFLUENT (2 % OXYGEN)
+ C5 EFFLUENT (3 % OXYGEN)
TEMPERATURE IN deg. C
220
200
180
160
140
120
100
80
60
40
20
0
10
20
30
40
50
60
70
80
90
100
% VOLUME EVAPORATED

FIGURE 24

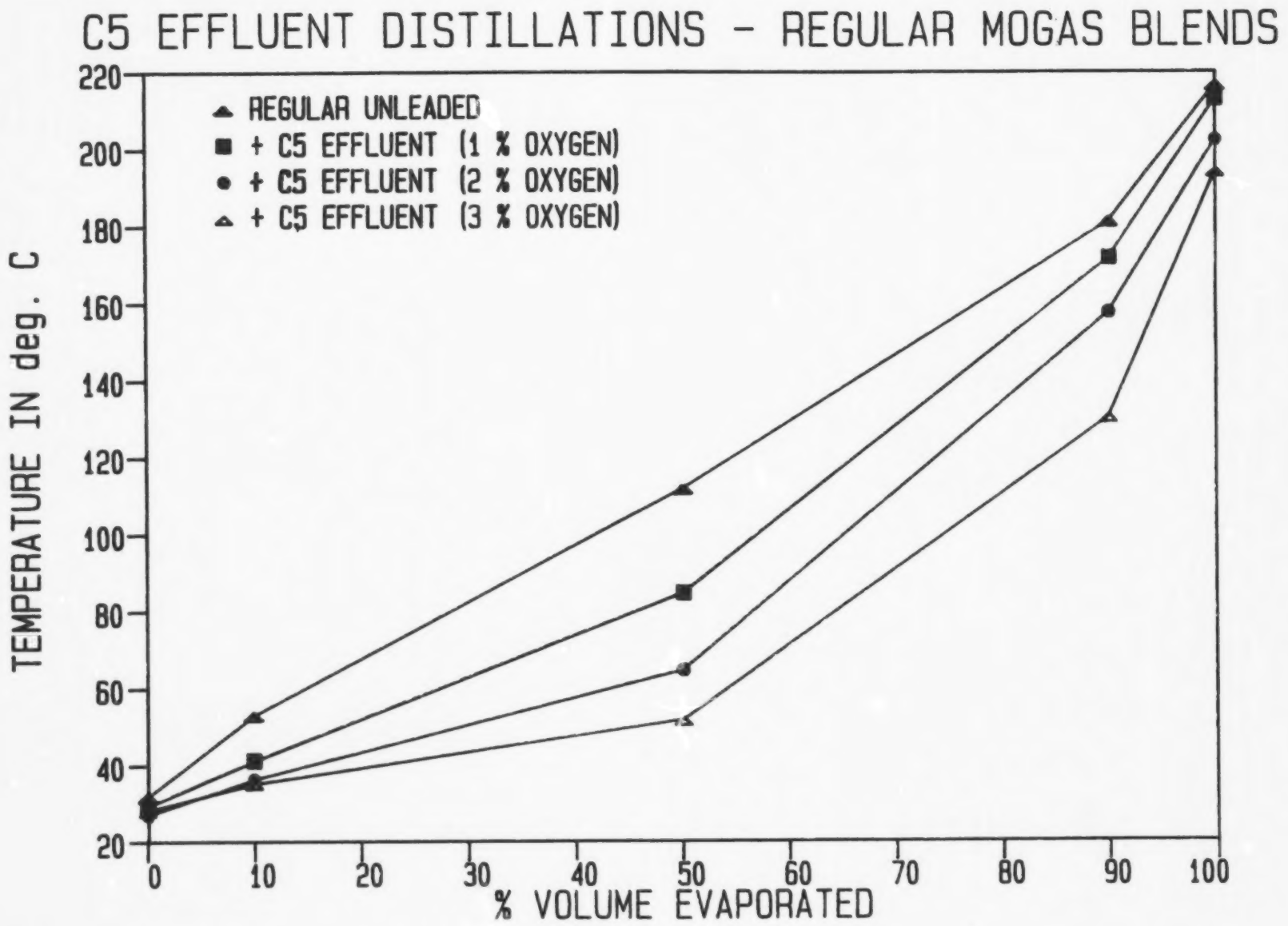

C5 EFFLUENT DISTILLATIONS - REGULAR MOGAS BLENDS
REGULAR UNLEADED
+ C5 EFFLUENT (1 % OXYGEN)
+ C5 EFFLUENT (2 % OXYGEN)
+ C5 EFFLUENT (3 % OXYGEN)
TEMPERATURE IN deg. C
220
200
180
160
140
120
100
80
60
40
20
0
10
20
30
40
50
60
70
80
90
100
% VOLUME EVAPORATED

FIGURE 25

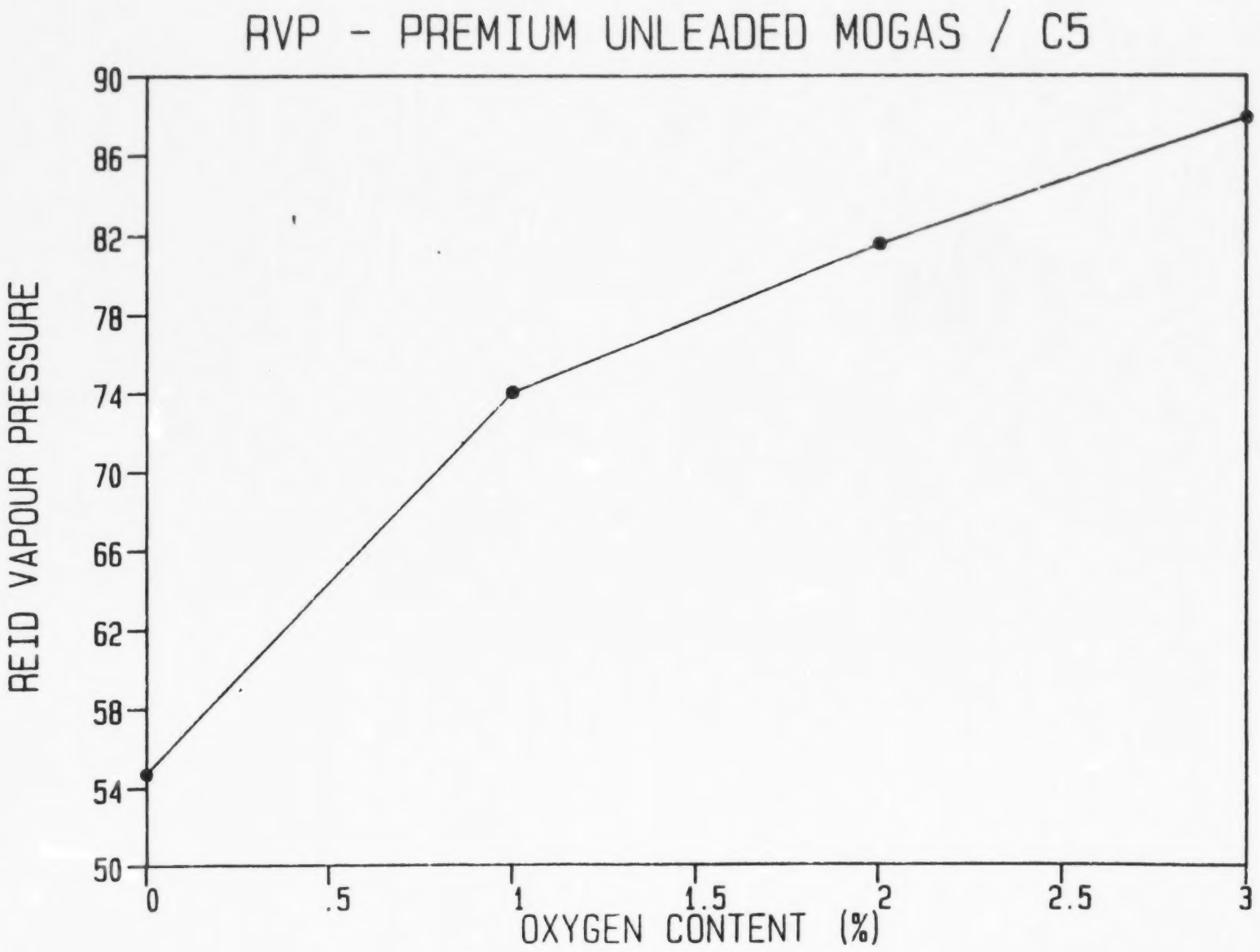

RVP - PREMIUM UNLEADED MOGAS / C5
REID VAPOUR PRESSURE
90
86
82
78
74
70
66
62
58
54
50
0
.5
1
1.5
2
2.5
3
OXYGEN CONTENT (%)

FIGURE 26

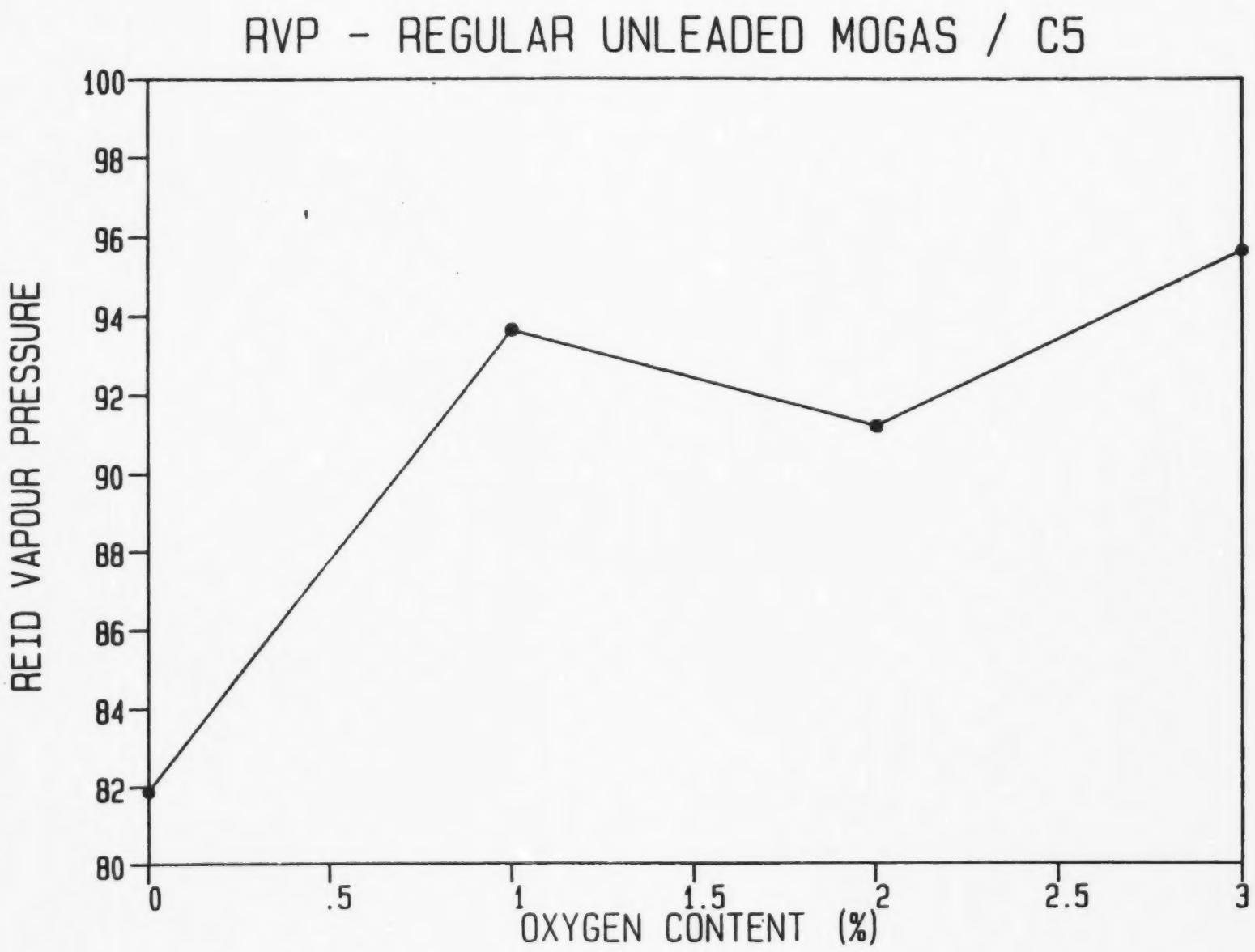

RVP - REGULAR UNLEADED MOGAS / C5
REID VAPOUR PRESSURE
100
98
96
94
92
90
88
86
84
82
80
0
.5
1
1.5
2
2.5
3
OXYGEN CONTENT (%)

FIGURE 27

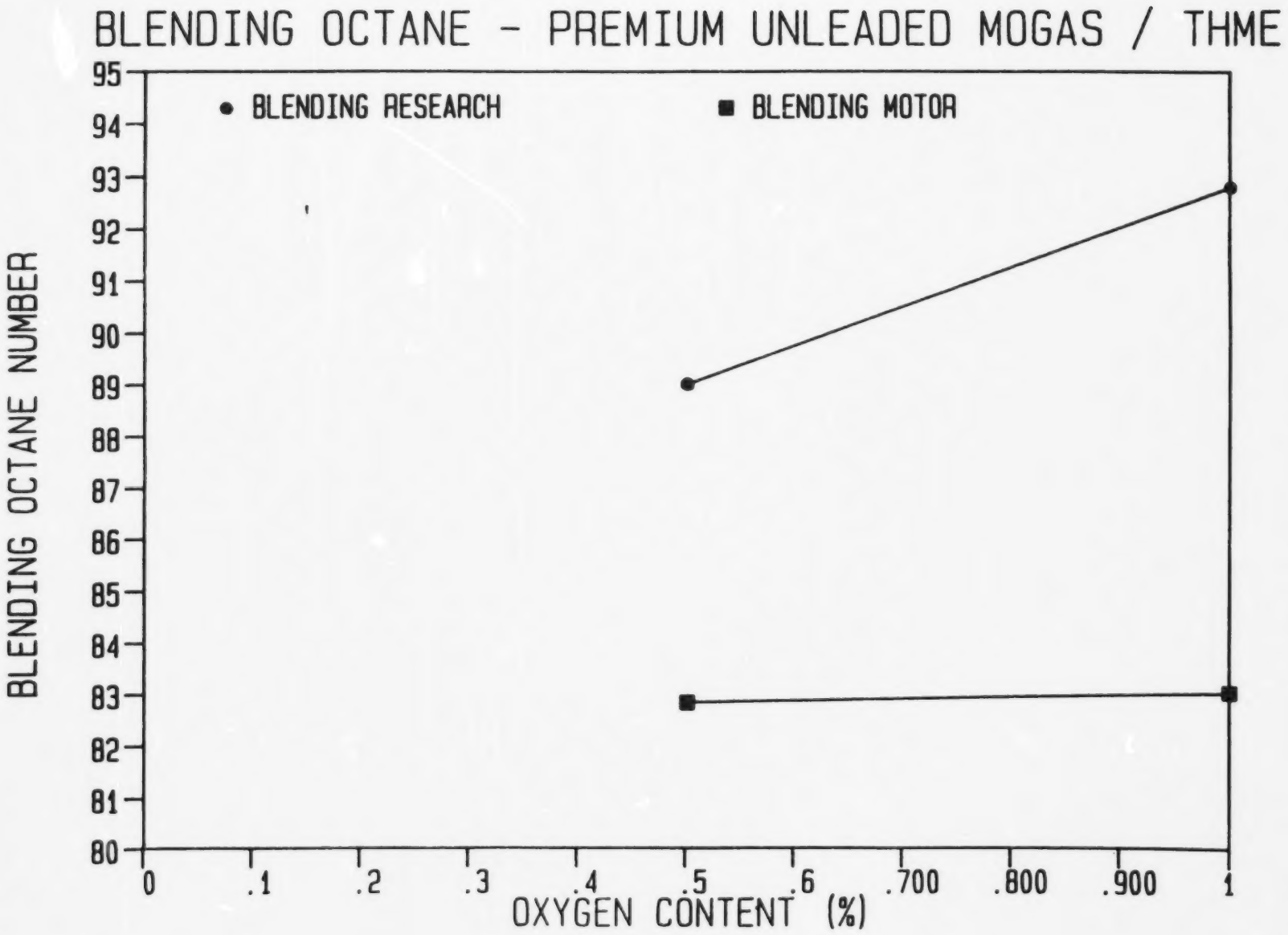

BLENDING OCTANE - PREMIUM UNLEADED MOGAS / THME
BLENDING RESEARCH
BLENDING MOTOR
BLENDING OCTANE NUMBER
95
94
93
92
91
90
89
88
87
86
85
84
83
82
81
80
0
.1
.2
.3
.4
.5
.6
.700
.800
.900
1
OXYGEN CONTENT (%)

FIGURE 28

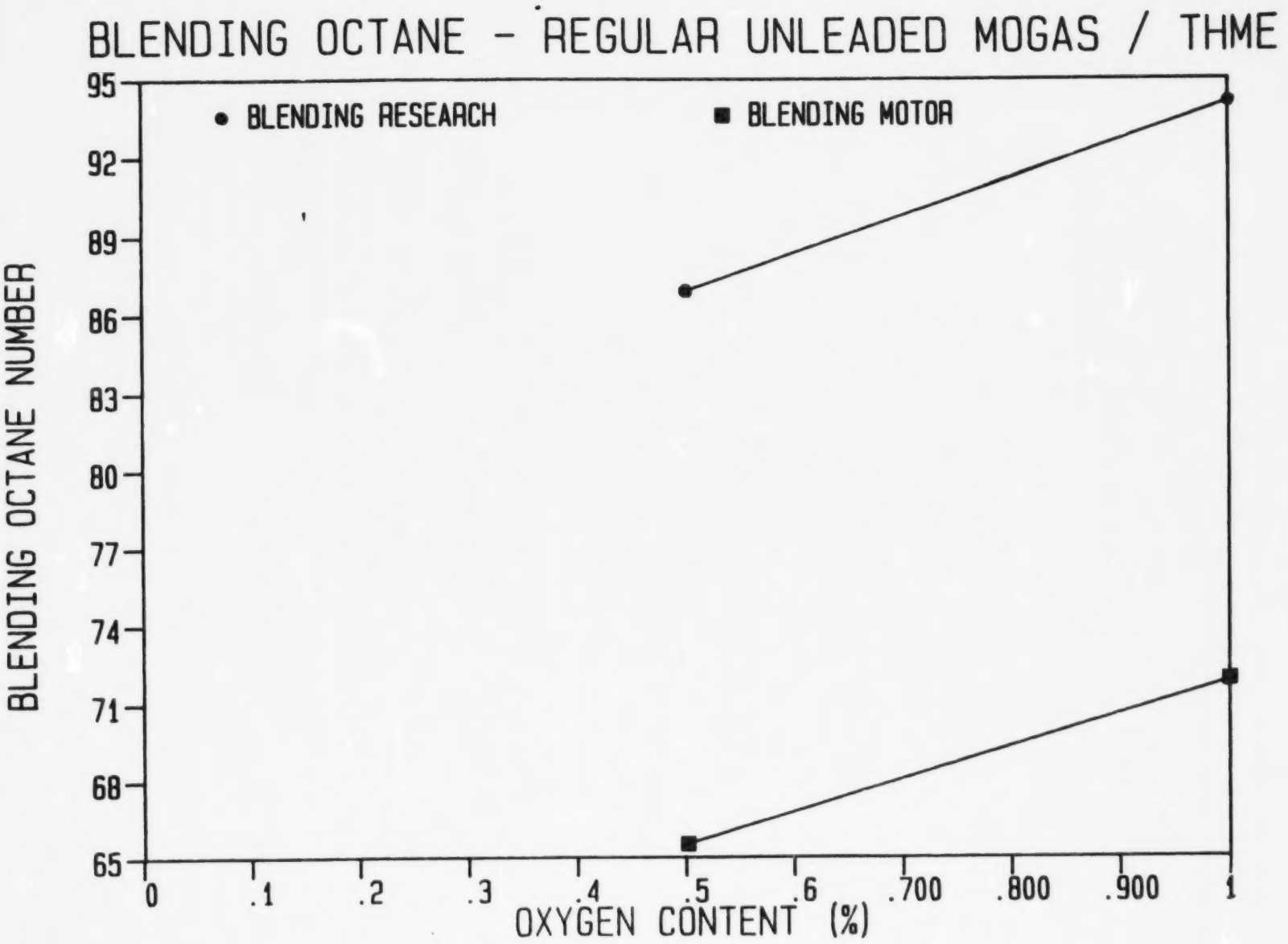

BLENDING OCTANE - REGULAR UNLEADED MOGAS / THME
BLENDING RESEARCH
BLENDING MOTOR
BLENDING OCTANE NUMBER
95
92
89
86
83
80
77
74
71
68
65
0
.1
.2
.3
.4
.5
.6
.700
.800
.900
1
OXYGEN CONTENT (%)

FIGURE 29

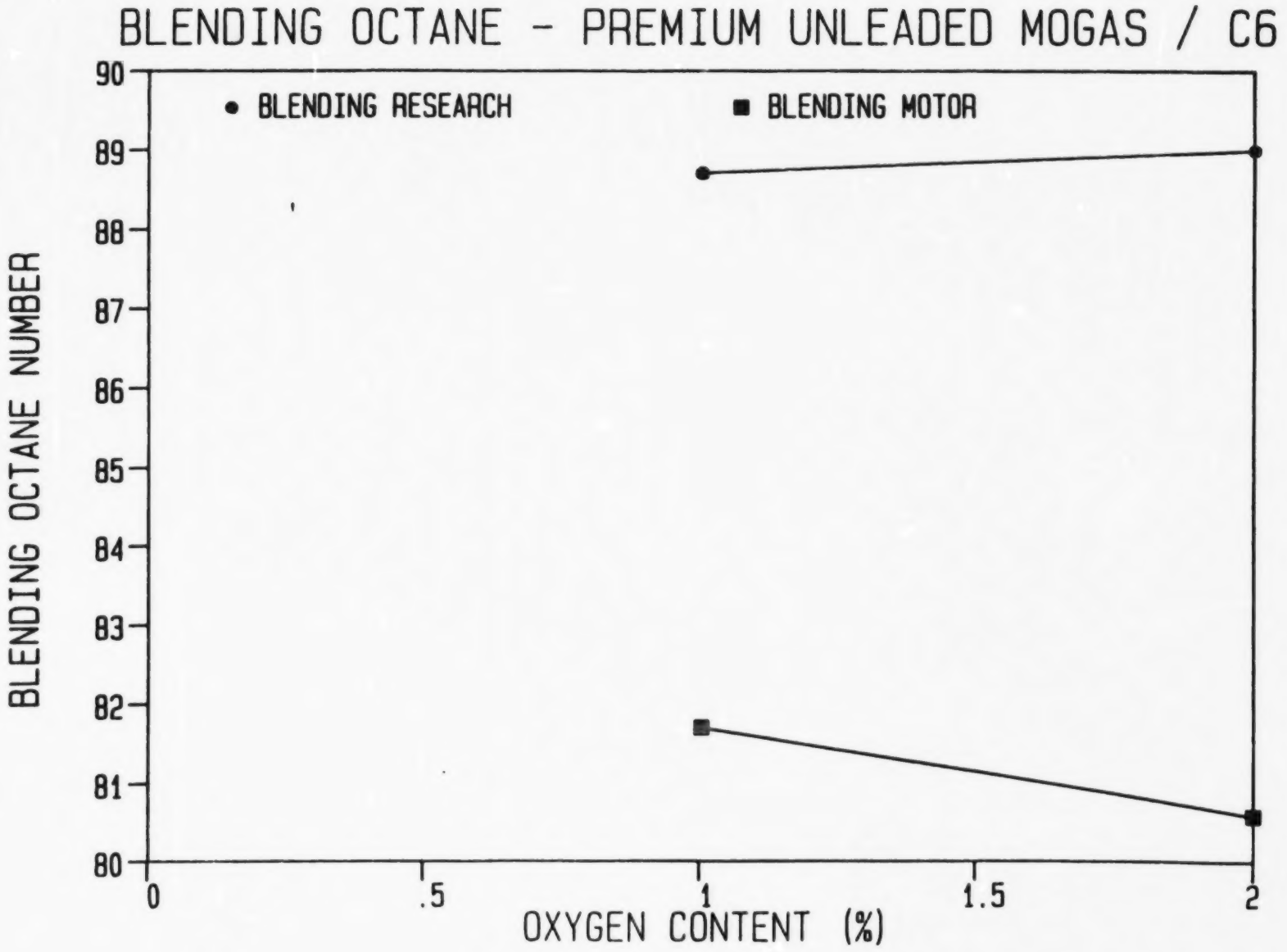

BLENDING OCTANE - PREMIUM UNLEADED MOGAS / C6
BLENDING RESEARCH
BLENDING MOTOR
BLENDING OCTANE NUMBER
90
89
88
87
86
85
84
83
82
81
80
0
.5
1
1.5
2
OXYGEN CONTENT (%)

FIGURE 30

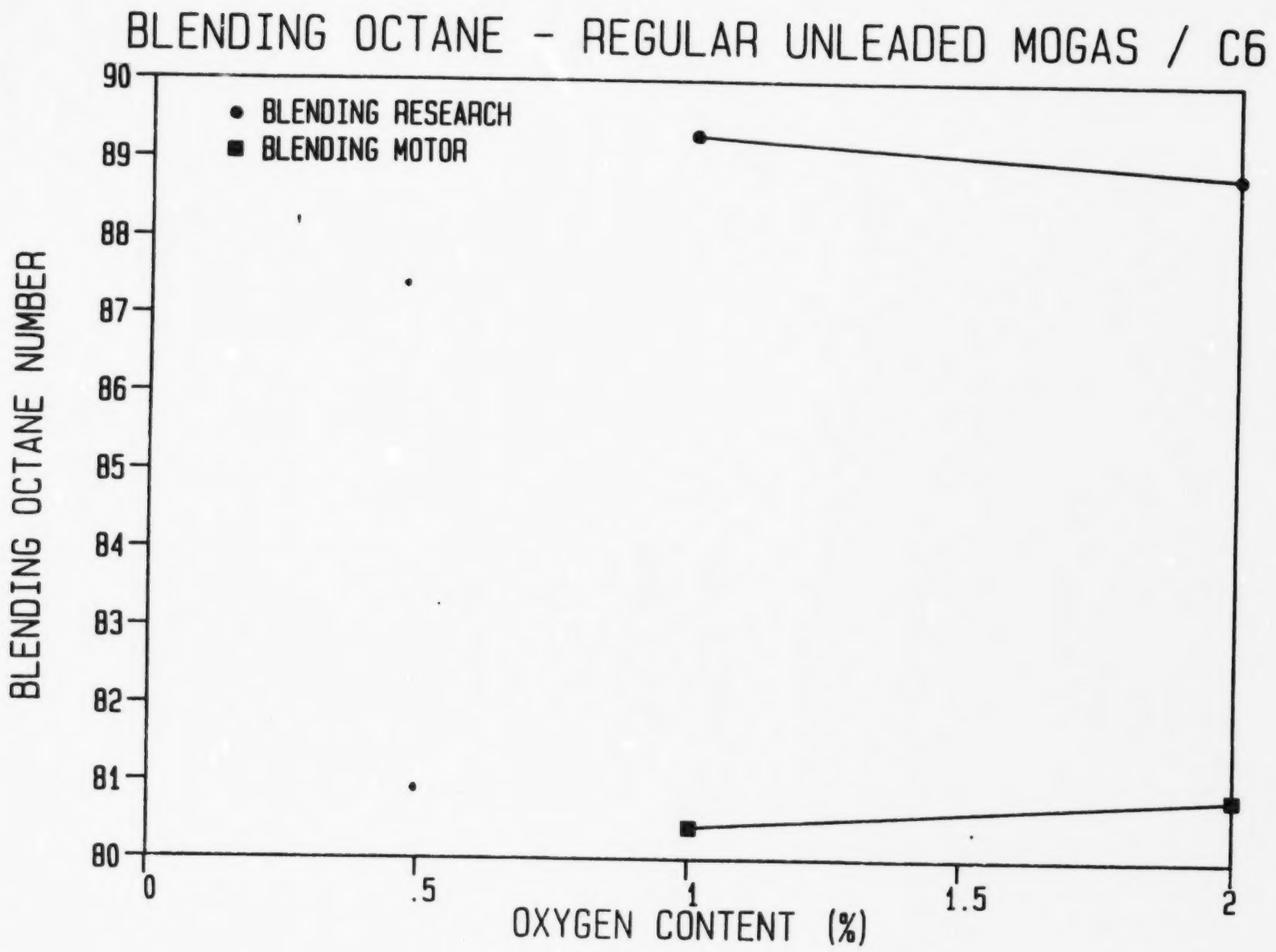

BLENDING OCTANE - REGULAR UNLEADED MOGAS / C6
BLENDING RESEARCH
BLENDING MOTOR
BLENDING OCTANE NUMBER
90
89
88
87
86
85
84
83
82
81
80
0
.5
1
1.5
2
OXYGEN CONTENT (%)

FIGURE 31

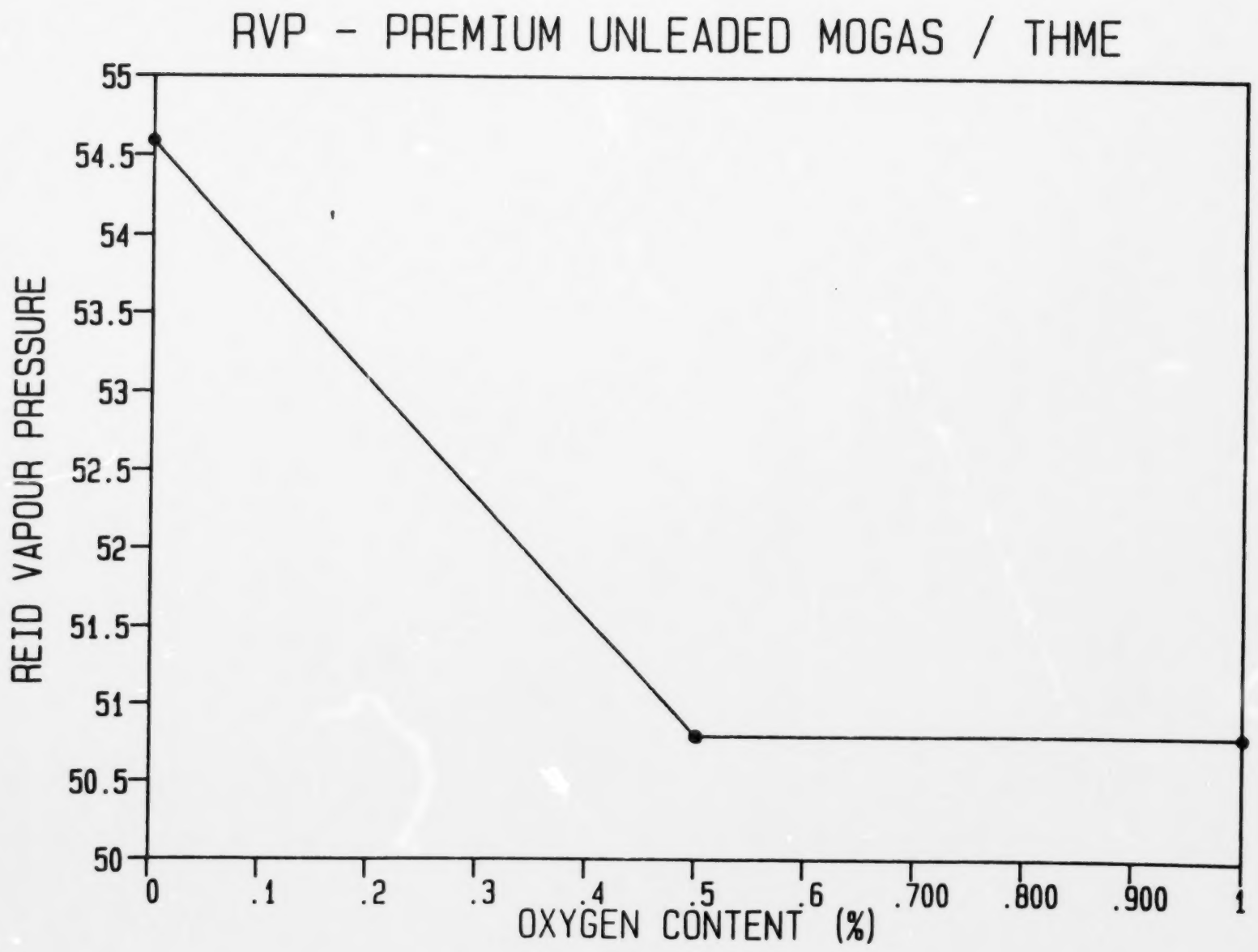

RVP - PREMIUM UNLEADED MOGAS / THME
REID VAPOUR PRESSURE
55
54.5
54
53.5
53
52.5
52
51.5
51
50.5
50
0
.1
.2
.3
.4
.5
.6
.700
.800
.900
1
OXYGEN CONTENT (%)

FIGURE 32

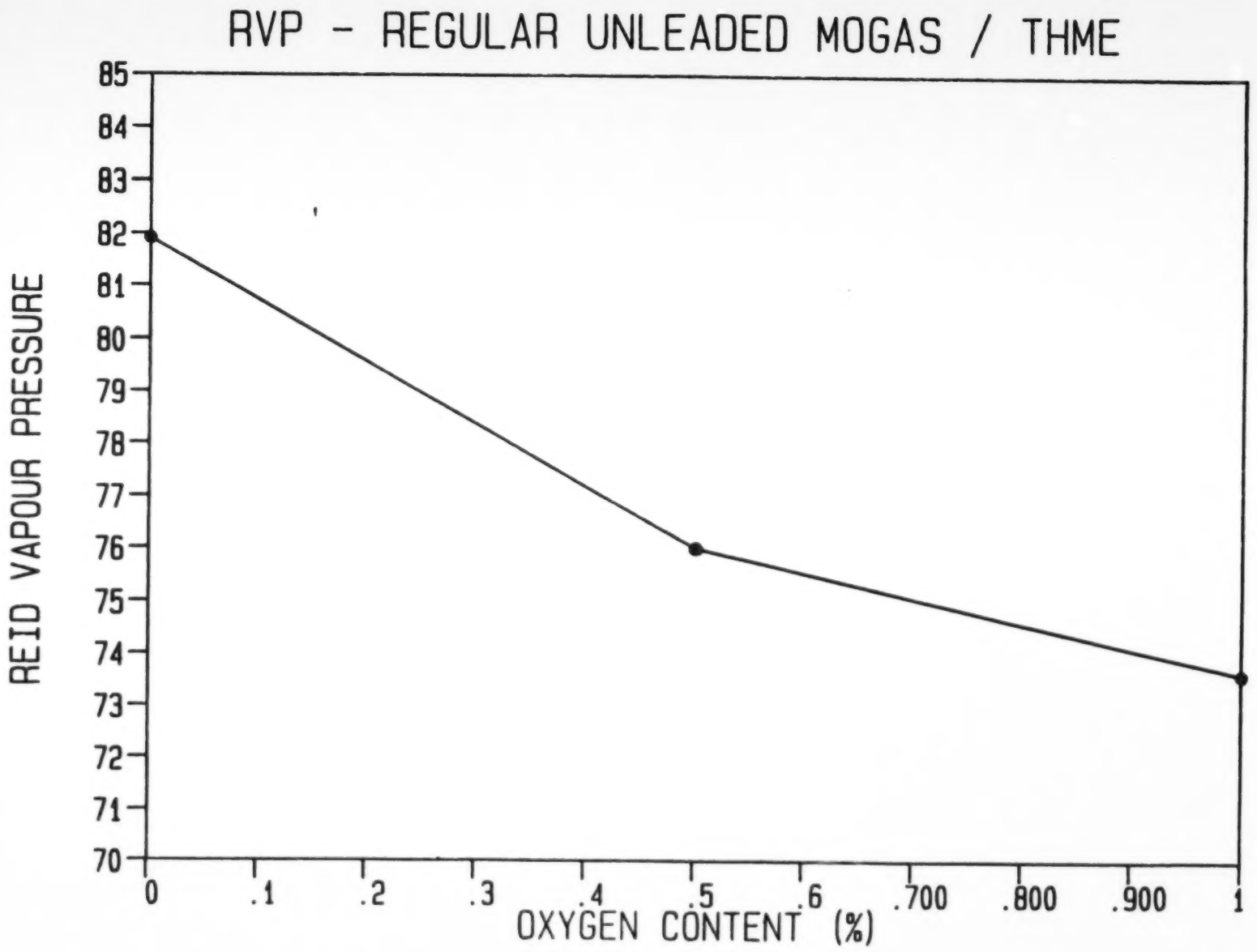

RVP - REGULAR UNLEADED MOGAS / THME
REID VAPOUR PRESSURE
85
84
83
82
81
80
79
78
77
76
75
74
73
72
71
70
0
.1
.2
.3
.4
.5
.6
.700
.800
.900
1
OXYGEN CONTENT (%)

FIGURE 33

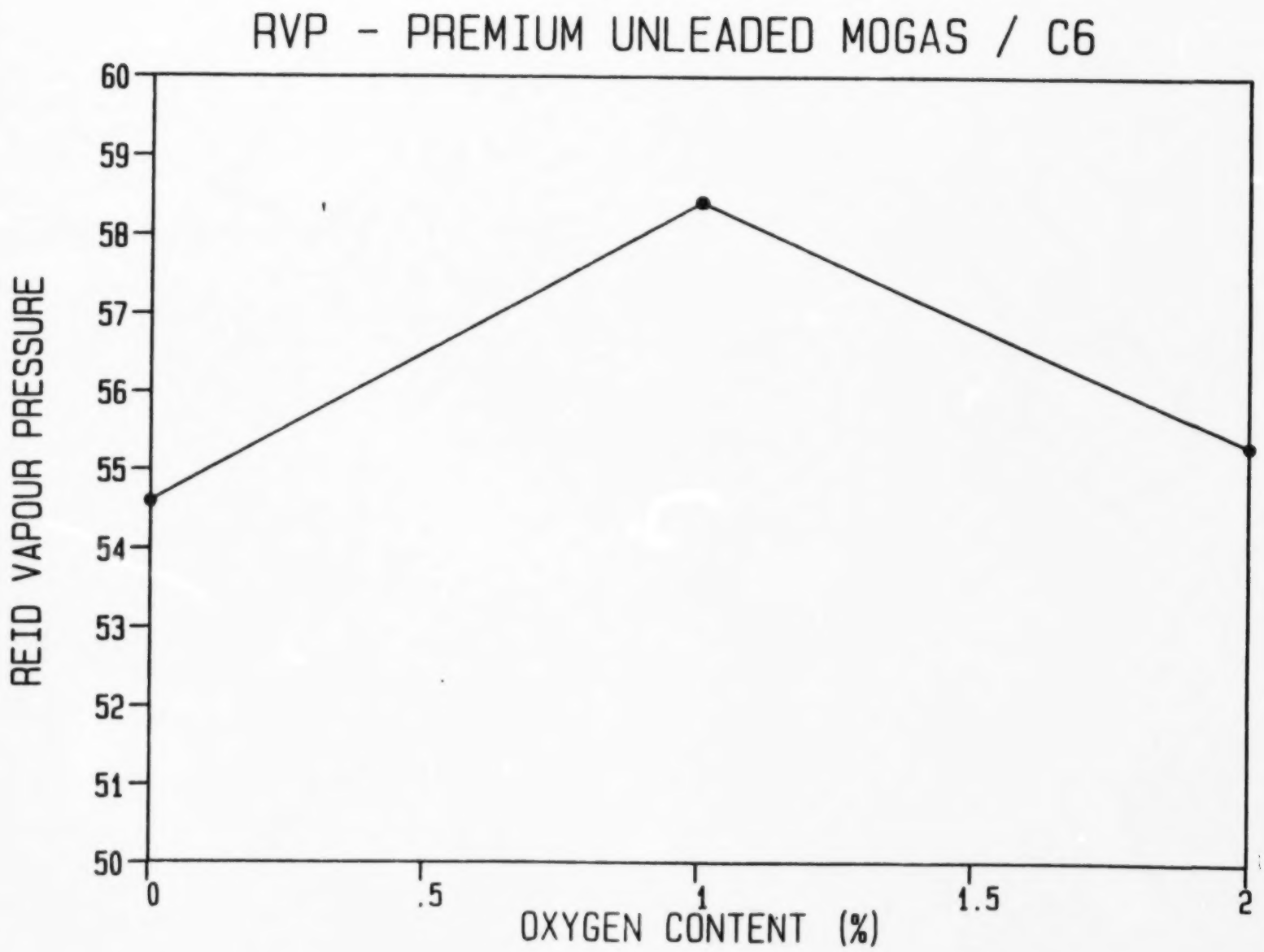
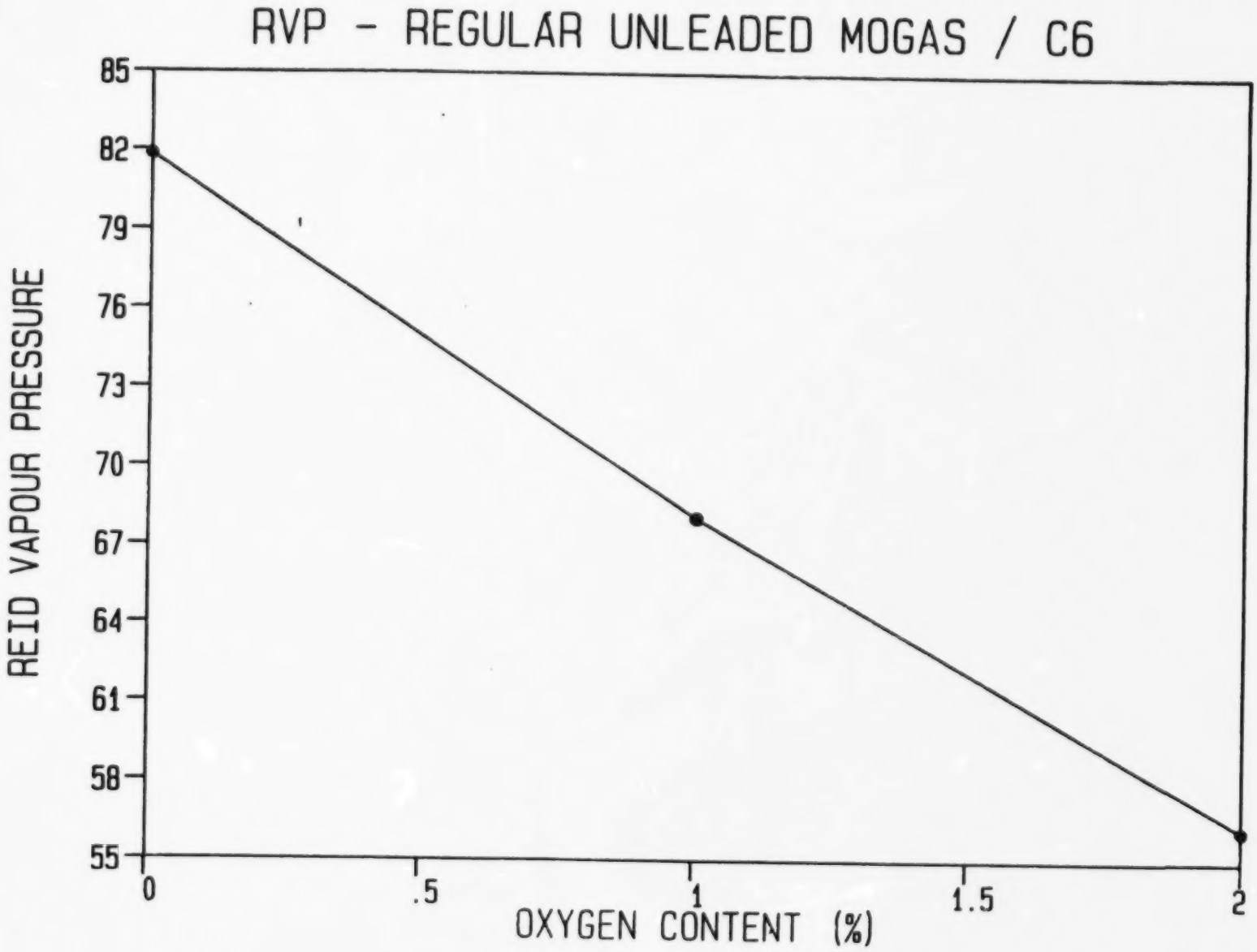

RVP - PREMIUM UNLEADED MOGAS / C6
REID VAPOUR PRESSURE
60
59
58
57
56
55
54
53
52
51
50
0
.5
1
1.5
2
OXYGEN CONTENT (%)

FIGURE 34


RVP - REGULAR UNLEADED MOGAS / C6
REID VAPOUR PRESSURE
85
82
79
76
73
70
67
64
61
58
55
0
.5
1
1.5
2
OXYGEN CONTENT (%)

A P P E N D I X

L.P. COMPUTER INPUT DATA

1. Base Case LP Input Data

i) Refining unit sizing as given in Table 1.
ii) Product demands (Table 1)
iii) Product specifications (Table 2)
iv) Lead = <0.29 g/L, MMT = <0.018 g/L
v) Current crude and product pricing

2. Hycarb Isomerization Unit LP Input Data

Capacity	= 1000 m^3/d
Cost	= $18,000,000 Canadian
Octane Delta	= 17
Octane Sensitivity	= 3
RVP Delta	= 2.5 psi
Yield	= 98% C_5 & C_6 product, 2% Fuel Gas loss
Fuel Function	= 0.012 FOE/bbl feed, 10 year catalyst life
H_2 Consumption	= 18 SCF/bbl feed

3. MTBE Process and Product Quality LP Input Data

Conditions are for a 4800 m^3/d FCCU, producing 12.1% l/v C_4 hydrocarbons containing 11.7% l/v isobutene

Reactor Temperature	= 100°C
$LHSV^{-h}$	= 1.5
Reactor Pressure	= 2.3 mPa
Conversion	= 80.0%
Methanol/Active Olefin Molar Ratio	= 1.1/1
Feed	= 11.7 l/v isobutene

C_4 Olefinic Hydrocarbon Feedstock

C_4 Olefinic Feed Stream	= 580 m^3/d
Active C_4 Olefin Feed (Isobutene)	= 67.9 m^3/d
C_4 Olefin Feed Reacted	= 54.3 m^3/d
Unreacted C_4 Olefin (Alkylation Feed)	= 525.7 m^3/d

Methanol Feed

Methanol Feed	= 32.0 m^3/d
Methanol Reacted (MTBE Formation only)	= 23.2 m^3/d
Methanol Loss + Side Reactions	= 3.0 m^3/d
Methanol Recycled	= 5.8 m^3/d
Methanol Consumption	= 26.2 m^3/d

Methyl Tertiary Butyl Ether

Reactor Product Total Volume	= 603 m^3/d
Loss in Total Volume	= 1.5%
MTBE Produced	= 68.4 m^3/d

Capital Costs

A cost of $2,500,000 has been estimated for the purchase and installation of necessary process equipment.

Operating Costs

Steam	= 96 mm BTU/h
Electrical	= 17.6 kw/h
Cooling Water	= 5000 L/h
Catalyst + Glycol	= $63,000/a
Methanol	= 9.3 ¢/L

3.1 MTBE Product Quality Data

RVP Blending Properties

When 5-10% MTBE is added to either a winter or summer grade of gasoline, approximately 1.0% l/v additional n-butane will be required to restore the vapour pressure to the original value.

Distillation Blending Properties

Up to 15% MTBE can be added to a normal gasoline without causing a distillation specification violation.

Octane Sensitivity for MMT

At 18 mg/L MMT, a response of 1 RON or 1 MON can be expected.

Octane Blending Numbers

MTBE (RON/MON)	= 116/101
n-Butane (RON/MON)	= 93.8/89.6 (31)
C_4 Alkylate (RON/MON)	= 93.0/90.0

The above C_4 process and product quality data was interfaced with the EMR-Hycarb forecast data.

4. TAME Process and Product Quality LP Input Data

Conditions are for a 4800 m^3/d FCCU, producing 10.0% l/v C_4 hydrocarbons containing 15.3 l/v isoamylenes.

Reactor Temperature	= 80°C
LHSV^{-h}	= 2.0
Reactor Pressure	= 1.7 mPa
Methanol/Active Olefin Molar Ratio	= 0.74/1
Feed	= 15.3% 1/v Isoamylene

C_5 Olefinic Hydrocarbon Feedstock

C_5 Olefinic Feed Stream	= 480 m^3/d
C_5 Olefinic Feed (Active C_5)	= 73.4 m^3/d
C_5 Olefin Feed Reacted	= 31.9 m^3/d
Unreacted C_5 Olefins	= 448 m^3/d

Methanol Feed

Methanol Feed	= 20.5 m^3/d
Methanol Reacted (TAME Formation only)	= 12.1 m^3/d
Methanol Loss + Side Reaction	= 2.5 m^3/d
Unreacted Methanol	= 5.9 m^3/d

C_5 Reactor Product

C_5 Reactor Product Volume	= 495.8 m^3/d
Tertiary Amyl Methyl Ether Produced	= 39.4 m^3/d
Loss in Total Volume	= 0.9%

Capital Costs

A cost of $500,000 has been estimated for the purchase and installation of necessary process equipment (one reactor and 2 pumps).

Operating Costs

Steam	= 52.8 mm BTU/h
Electrical	= 2.5 kW/h
Catalyst	= $30 000/a
Methanol	= 9.5¢/L

4.1 TAME Product Quality Data

RVP Blending Properties

When 10% C_5 reactor product is added to gasoline approximately 1.5% l/v less n-butane will be required to maintain the original vapour pressure.

Distillation Blending Properties

Up to 25% C_5 reactor product can be added to a normal gasoline without causing a distillation specification violation.

Octane Blending Characteristics

TAME (RON/MON)	= 106/99
n-Butane (RON/MON)	= 93.8/89.6
C_5 Reactor Feed 25-50°C (RON/MON)	= 95.3/84.0
C_5 Reactor Product (RON/MON)	= 96.3/85.8
C_6 Feed Stream (RON/MON)	= 92.5/80.6

Octane Sensitivity for MMT

At 18 mg/L MMT, a response of 1 RON or 1 MON can be expected.

The above-C_5 process and product quality data was interfaced with the EMR-Hycarb forecast data.

TABLE 1

ETHER ECONOMIC EVALUATION

Refinery Unit Sizing

	m^3/SD	Barrels/SB
Crude Unit	16 000	100 000
FCCU	4 800	30 000
Reformer	3 500	22 000
Alkylation	1 000	6 300

Annual Product Demands

	m^3/day
Leaded Regular	730
Unleaded Regular	5 110
Unleaded Premium	1 460
Jet B	150
Jet A	810
Kero/Stove	90
Diesel Winter	1 750
Summer	1 170
Light Furnace Oil	1 700
-	12 970

(1) HFO, LPG, Fuel/Gas produced to balance refinery operations.
(2) Demands are Hycarb Study, Product Slate "B", which approximate mid 1990's demands (1).

TABLE 2

ETHER ECONOMIC EVALUATION

GASOLINE SPECIFICATION

Octane Specifications	Leaded[1] Regular	Unleaded[2] Regular	Premium[2] Unleaded
Average Octane, (R+M)/2, min			
Prairies	88.3	88.3	90.8
Other Locations	89.8	89.0	91.8

Volatility Specifications	Current Min.	Current Max.	Proposed[3] Min.	Proposed[3] Max.
RVP, psia				
Summer	-	11.0[4]	-	11.5
Average	-	13.0[4]	-	13.6
Winter	9.0[4]	15.0[4]	10.0	15.5
Boiling Point at 50% off, °C				
Summer	80[5]	118[4]	80	120
Average	80	116	73	115
Winter	80	113[4]	65	110
% Off at 70°C[6]				
Summer	20	40	15	40
Average	20	40	20	46
Winter	20	40	25	52
% Off at 100°C[6]				
Summer	35	65	35	65
Average	35	65	40	71
Winter	35	65	45	77

Notes: (1) Lead content <0.77 g/L in 1985, <0.29 g/L in 1987.
(2) Manganese content <0.018 g/L.
(3) Proposed CGSB specification for oxygenated gasoline.
(4) Current CGSB specification, CAN2 - 3.1 and CAN2 - 3.5
(5) Based on current ASTM specification D439.
(6) As used in refinery LP model.

Source: EMR Hycarb Report (1)

BLENDING OCTANE VALUES FOR C_5 REACTOR EFFLUENT AND FEEDSTOCK

The C_5 reactor feedstock was determined to have octane numbers of 95.3 RON and 84.0 MON.

From Tables 24 and 25, the average blending RON for the six blends was 96.8 and the average blending MON for the six blends was 86.8.

The C_5 reactor effluent used in the blending study was the product from a 60.8% conversion of isoamylenes to TAME and contained

14.8% vol TAME
1.9% vol Methanol — 18.6% vol
1.9% vol Isopropanol

For a C_5 reactor effluent from only a 43.5% vol conversion of isoamylenes to TAME, the proportional amounts of TAME, etc. are:

X 14.8% TAME = 10.6% TAME

11.8% vol

X 1.9% Methanol = 1.2% Methanol

Now the two isoamylenes are present in a thermodynamic equilibrium of 30% 2-Methyl Butene-1 and 70% 2-Methyl Butene-2

2-Methyl Butene-1 has octane numbers of 100.1 RON/81.9 MON
2-Methyl Butene-2 has octane numbers of 97.3 RON/84.7 MON

The effect of the unreacted isoamylenes is

RON Δ = 106 - (0.3 X 100.1 + 0.7 X 97.3)
= 106 - 98.1 = 7.9

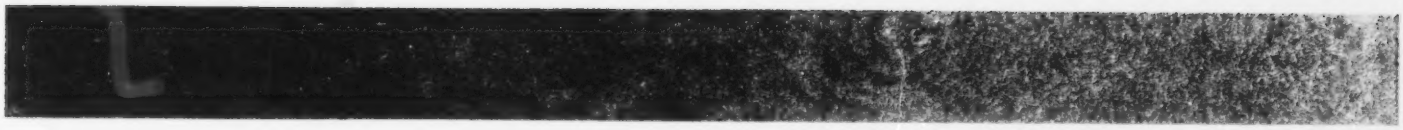
MON Δ = 99 - (0.3 X 81.9 + 0.7 X 84.7)
= 99 - 83.9 = 15.1

Therefore the blending octane numbers for the C_5 reactor effluent at the 43.5% vol conversion of isoamylenes is

$$RON = 96.8 - 7.9\ (0.186 - 0.118) = 96.8 - 0.5 = \underline{96.3}$$

$$MON = 86.8 - 15.1\ (0.186 - 0.118) = 86.8 - 1.0 = \underline{85.8}$$

The two calculated values were used in the linear program product quality input data for C_5 reactor effluent.



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